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REVISION OF THE ATOMIC WEIGHT OF GOLD.[1]

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Until lately gold ranked among the elementary substances of which the general properties had been well ascertained, but in regard to the atomic weights of which our knowledge was least satisfactory. That this constant should be determined as accurately as possible for gold was desirable in view of its bearing on the precise place assigned the metal in the "periodic" classification of the elements based on the ideas of Newlands, Odling, Mendelejeff, and L. Meyer. Furthermore, an exact knowledge of the atomic weight of gold might be conveniently applied in the determination of the atomic weights of some of the other elements. A practical laboratory reason for desiring to possess a trustworthy value for this constant was also presented by the facility with which gold compounds of many organic substances may be prepared, and the ease with which their composition may be ascertained by simple ignition in the air and weighing of the residual gold, the results leading to a knowledge of molecular composition when the atomic value of the weight of the metal obtained is assumed to be known.

For the last three years and a half I have been occupied, during a large part of such time as has been available for original work,

[1] From the Philosophical Transactions of the Royal Society of London, **180** (1889), A, pp. 395-441.

in devising and carrying out experiments aiming at the redetermination of the constant in question. The difficulties met with have been greater than were at first looked for, and have led to much time and labor being consumed in attempts to overcome them. About two years ago, when this work was already well under way but still in progress, there appeared the results of experiments aiming at the same end, by Krüss in Germany and by Thorpe and Laurie in England—experiments made with the care and accuracy of modern methods, and apparently deserving of much confidence. My own work, however, was continued, as we cannot have too many careful independent determinations of atomic weights by different workers, and as I had used to a considerable extent other processes than those on which the newly published determinations were based, while the chemists named had employed, in the main, one and the same method. A preliminary notice of my work was read in the Chemical Section of the British Association at the Manchester meeting of 1887. The details of my experiments and the results which I have reached are now laid before the Royal Society.

Earlier Determinations of the Atomic Weight of Gold.

In the work of L. Mulder, "Historisch-kritisch Overzigt van de Bepalingen der Æquivalent-Gewigten van 24 Metalen," Utrecht, 1853, and in the recent papers of Krüss and of Thorpe and Laurie, there are abstracts of reports upon a number of experiments by chemists of the earlier part of this century, bearing on the value to be assigned to the atomic weight of gold, such as those of Proust,[1] Richter,[2] Dalton,[3] Thomson,[4] Oberkampf,[5] Pelletier,[6] Figuier,[7] and Javal;[8] but of these none deserve any attentive consideration at the present day, the methods used having in some cases been such that accurate results could not be expected from them, and the actual figures obtained in other cases differing so widely from each other that no importance can be attached to them.

Before the year 1887 but two chemists—Berzelius and Levol—had published the results of experiments furnishing fairly admissible data for calculating the atomic weight in question.

[1] Journal de Physique **62** (1806), 131; N. Gehlen, Journal **1** (1806), 477.
[2] Schweigger, Journal **7**, (1813), 43.
[3] New System, Part 2 (1810), 253.
[4] First Principles **1** (1825), 440.
[5] Annales de Chimie **80** (1811), 140.
[6] Ib. **15** (1820), 5, 113.
[7] Ib. **19** (1821), 177.
[8] Ib. **17** (1821), 337; Schweigger, Journal **33** (1821), 238.

A. *Experiments of Berzelius*, 1813.[1]—The method adopted was the precipitation of a solution of auric chloride by metallic mercury, determining the quantities of mercury dissolved and gold thrown down. In the original paper but a single experiment is reported, but later the author appears to have made a second,[2] so that for the two Meyer and Seubert, in their recalculation of the atomic weights of the elements,[3] give as the sums of the amounts of mercury and gold found to be equivalent to each other 24.240 grams of the former and 15.912 grams of the latter. Taking these quantities to represent the ratio between the weights of three atoms of mercury and two atoms of gold, we have for the weight of the single atom of the latter (H = 1):

If we assume Hg = 199.8 (L. Meyer and Seubert),[3]	196.73
" " " = 199.712 (F. W. Clarke),[4]	196.65

This method recommends itself as advantageous on several grounds, and the experiment deserves repetition as soon as the atomic weight of mercury becomes known with greater certainty than at present. But until this condition is fulfilled, the result for gold cannot be depended upon as of the first rank in exactness. In any renewed attempt to apply this method several questions would have to be examined as to the precise nature of the solution used, and of the reaction itself.

[Berzelius[5] also precipitated gold by means of a known quantity of phosphorus from a solution of the chloride used in excess, and his results, as calculated by F. W. Clarke,[6] lead to the atomic weight 195.303 for gold; but this process appears ill adapted to give very exact results, even in such hands as those of the great Swedish chemist, and the value obtained is certainly too low in the light of more modern researches.]

B. *Experiments of Berzelius*, 1844.[7]—In these experiments potassium auri-chloride, which, it was found, could not be completely dried without loss of chlorine, was ignited in hydrogen, and the residue was treated with water to dissolve potassium

[1] Stockholm, Kgl. Vetensk. Akad. Handl., 1813, 185.

[2] Berzelius, Lehrbuch **3**, p. 1212, str. 70.

[3] Lothar Meyer u. Karl Seubert, Die Atomgewichte d. Elemente aus d. Originalzahlen berechnet, Leipzig, 1883, 191.

[4] "The Constants of Nature," Smithsonian Miscellaneous Collections, Washington, D. C.

[5] Berzelius, Lehrbuch, 5. Aufl. **3**, 1188.

[6] "The Constants of Nature," Smithsonian Miscellaneous Collections, Washington, D. C.

[7] Berzelius, Lehrbuch, 5. Aufl. **3**, 1212.

chloride, the quantity of which was determined, as well as that of the metallic gold left undissolved. Five experiments were made, and the aggregate amounts obtained of potassium chloride and gold were 3.7800 grams and 9.9685 grams respectively. These figures, if we assume K = 39.03 and Cl = 35.37, give for the atomic weight of gold 196.20, the lowest result from one of the individual experiments being 196.11, and the highest 196.27.

Among possible sources of error in this process we may note as deserving consideration the conceivable retention by the potassium auri-chloride of hydrogen auri-chloride, and the difficulty of directly determining with accuracy the potassium chloride extracted by water. The former would lead to a higher result for gold than should be obtained; the latter might either give too low a result in consequence of imperfect drying, or too high if there were partial loss by volatilisation, either during the ignition in hydrogen or in subsequently recovering the potassium chloride from solution. The quantities of material used were smaller than is probably desirable.

C. *Experiments of Levol*, 1850.[1]—A weighed quantity of gold was dissolved as auric chloride, the metal reduced from the solution by means of sulphur dioxide, and the sulphuric acid formed was determined as barium sulphate. In two experiments, reported as giving exactly the same result, 1 gram of gold gave 1.782 gram of barium sulphate. Hence, if Ba be taken = 136.86, S = 31.98, and O = 15.96, we have for the atomic weight of gold the number 195.86.

Of the sources of error to which this method is liable probably the most important are atmospheric oxidation of sulphurous to sulphuric acid and imperfect washing out of soluble compounds of barium from the barium sulphate. Both would tend to give too low a result for gold.

For all these earlier experiments details are wanting as to the exact mode of purification of the gold and other materials used, and in the weighings there appears to have been no correction introduced for atmospheric buoyancy; the results doubtless represent apparent, not absolute, weights.

[There is also to be quoted the statement of Julius Thomsen,[2] that he found in hydrogen brom-aurate ($AuBr_3.HBr.5H_2O$) 32.11 per cent. of gold and 52.00 per cent. of bromine, from which he

[1] Annales de Chimie [3] **30**, 355.

[2] J. prakt. Chem. **13** (1876), 345.

concluded that Au = probably about 197. Taking Br = 79.76, and calculating from the ratio of Br_4 : Au, the number is 197.01.]

Recent Careful Determinations of the Atomic Weight of Gold.

A. *Experiments of Gerhard Krüss*, 1886.[1]—The author has described in detail the means resorted to for the preparation of pure metallic gold, and especially for its separation from silver and the metals of the platinum group, with an account of the spectroscopic examination of the gold employed. He has then given a full account of: *a.* His determinations of the gold and chlorine (the former reduced by a stream of sulphur dioxide; the latter precipitated and weighed as silver chloride) in a neutral solution of auric chloride, prepared by the action of water on the so-called auro-auric chloride (Au_2Cl_4),[2] itself prepared by the direct action of chlorine on metallic gold; *b.* Like determinations of gold and chlorine in sublimed auric chloride, made by direct action of the elements on each other with careful regulation of the temperature; *c.* Determinations of the gold in a weighed quantity of potassium auri-bromide ($KAuBr_4$), the metal in some experiments reduced from a solution of the salt by sulphurous acid, in others reduced from the dry salt by heating in a stream of hydrogen; *d.* Determinations of the gold and bromine (the former thrown down by sulphurous acid; the latter precipitated as silver bromide) in the same salt, potassium auri-bromide; *e.* Determinations of the loss of weight (representing 3 atoms of bromine for 1 of gold) undergone by heating potassium auri-bromide gradually to 320° C., towards the end in a stream of hydrogen; *f.* Determinations of the quantity of potassium bromide recovered from the residue left in the experiments of *e* by treatment of this residue with water, separation of the metallic gold, careful evaporation of the liquid, and final cautious heating of the potassium bromide over a free flame. In the experiments of series *a* account was taken of the somewhat different processes of purification of the gold used, but, no corresponding differences being observable in the results obtained, no further record was made in the remaining series of the history of the gold used in these.

[1] Ann. Chem. (Liebig) **238**, 30; and separate publication, G. Krüss, Untersuchungen über das Atomgewicht des Goldes, München, 1886.

[2] Krüss has in a later paper (Ber. d. chem. Ges. **20**, 2634) denied the existence of auro-auric chloride as a definite compound, but admits that the substance so described by Julius Thomsen yields on treatment with warm water a solution of pure neutral auric chloride, with separation of metallic gold.

After correction of the weighings for atmospheric buoyancy in such cases as seemed to the author to involve a correction worth noticing, the following results were calculated from the figures obtained, these figures agreeing in general closely with each other in each series:

Series	*a*.	Mean of	8	experiments.	At. weight of gold	= 196.622
"	*b*.	"	4	"	"	= 196.143
"	*c*.	"	9	"	"	= 196.741
"	*d*.	"	5	"	"	= 196.743
"	*e*.	"	4	"	"	= 196.619
"	*f*.	"	4	"	"	= 196.620

Leaving out the results of series *b* on the ground of the very small quantity of sublimed auric chloride available, and the considerable discrepancy of one of the results (that in which most material was used) from the rest, the author calculates from the remaining 30 experiments the general mean 196.669; but, taking into account the greater or less closeness of agreement of the figures obtained by the several methods, he comes to the conclusion that 196.64 may better be assumed as the true atomic weight of gold. In these calculations Ag was assumed = 107.660, Cl = 35.368, Br = 79.750, and K = 39.040.

As regards possible sources of constant error in Krüss's experiments, it may be observed that—

1. In series *b* very small quantities of sublimed auric chloride were used—the whole amount available for all four experiments being only about seven-tenths of a gram—and it is probable that a little free chlorine may have been physically retained by the chloride in spite of the long-continued passage over it of dry air. The experiment in which the largest quantity of material was used gave the atomic weight = but 194.79. On these grounds the author himself excludes the series from consideration in calculating his general mean.

2. In series *c*, *d*, and *e* the evidence is pretty strong, but perhaps not conclusive, to show that potassium auri-bromide can be rendered absolutely dry by exposure to air in a vessel containing phosphorus pentoxide, either at ordinary or higher temperatures, without, at the same time, undergoing any loss of bromine. The attainment of constant weight by the salt does not positively prove the entire removal of water. If moisture were retained the atomic weight of gold found would be brought out lower than it should be.

3. Krüss himself observed that in all cases in which he dissolved potassium auri-bromide in water a small residue of metallic gold was left, and, determining in a single experiment the amount of this (about .05 per cent.), he used it as a correction for all his results. As pointed out by Thorpe and Laurie,[1] this partial decomposition of the salt was probably due to the action of dust from the air. If the results obtained from the solution were used, without any correction, to establish the atomic weight of gold, the tendency would of course be to a value lower than the truth. Although the correction introduced is small, it can hardly be supposed that it should be taken as constant in amount in all the experiments.

4. In series *e* it may be questioned whether traces of potassium bromide may not have been volatilised at the highest temperature used, or the residual potassium bromide may not have, to a small extent, exchanged bromine for oxygen while heated in air (before the use of the stream of hydrogen), the latter change being one to be guarded against whenever haloid salts are strongly heated in the presence of free oxygen. The tendency in both cases would be to a lower atomic weight for gold.

5. In series *f* there was risk of slight loss of potassium bromide during filtration and evaporation of its solution, and during exposure of the salt to the heat of a free flame, when there might possibly have been again slight replacement of bromine by oxygen, thus causing the atomic weight sought to come out too high, or else, on the other hand, risk of imperfect drying, which would give too low a value for the atomic weight in question.

On the whole it seems probable that the tendency of most of the constant errors to be suspected in connection with Krüss's experiments—experiments carried out with remarkable patience, skill, and apparent freedom from merely "fortuitous" errors—was in the direction of an atomic weight for gold somewhat below, rather than above, the true value.

B. *Experiments of Thorpe and Laurie*, 1887.[2]—In these experiments potassium auri-bromide was used, and determinations were made: *a*. Of the weight of the residue left on heating the salt over a Bunsen flame till bromine ceased to be given off (this residue consisting of metallic gold and potassium bromide), and

[1] Chem. Soc. Journ., Dec., 1887, p. 866.
[2] Ibid., June, 1887, p. 565, and Dec., 1887, p. 866.

the weight of the gold left by such residue after all potassium bromide had been washed out of it by water; *b*. Of the weight of silver necessary to be added as nitrate to the solution of potassium bromide obtained in *a* in order to just precipitate the bromine present; *c*. Of the weight of the silver bromide so precipitated. All suitable experimental precautions seem to have been taken, and the weighings were corrected for atmospheric buoyancy. The individual results in each series agreed with each other even more closely than in Krüss's research.

The results obtained were as follows, using in calculation the numbers Ag = 107.66, Br = 79.75, and K = 39.03:

Series *a*.	Mean of 8 experiments.			At. weight of gold	=	196.876
" *b*.	" 9	"	"	"	"	=	196.837
" *c*.	" 8	"	"	"	"	=	196.842

The general mean of these values, giving equal weight to the different series, is 196.852.

As regards possible sources of constant error specially belonging to these experiments, it is to be noticed—

1. There is an advantage, as observed by the authors themselves, over the greater part of the experiments of Krüss, in the nature of the relations employed not requiring that the potassium auribromide should be perfectly dry, the exact quantity of the original salt not needing, in fact, to be known.

2. In series *a* it is conceivable that there might have been slight volatilisation of potassium bromide, or interchange in it to a small extent of bromine for oxygen, during the heating of the original salt, or retention of traces of potassium bromide by the metallic gold when washed—the latter but little probable. Any of these defects, if existing, would cause the method to give a higher value for Au than the true one.

3. In series *b* the probability seems to be in favor of not quite the whole of the original potassium bromide being actually used, and minute loss of silver solution having perhaps occurred, so that rather more of this solution was counted as used than the true quantity. If so, the former defect would tend to raise, the latter to lower, the atomic weight of gold.

4. In series *c*, in view of the evidence adduced to prove complete drying of the silver bromide, it is more likely that its weight as obtained was below, rather than above, the truth. Hence we

should suspect, if any constant error exist, that it would rather tend towards an unduly high value for Au.

On the whole, there seems to be less reason to fear sources of constant error of any considerable amount in connection with the experiments of Thorpe and Laurie than with those of Krüss, and the drift is in the opposite direction, tending rather to give too high than too low a value for the atomic weight to be determined.

It should be mentioned that Krüss[1] has claimed that in the potassium auri-bromide used by Thorpe and Laurie there was probably as much free gold as he considered to exist in the salt used by himself, and on this assumption has calculated that the three series of experiments by the English chemists should, if corrected on this account, lead to the numbers 196.616, 196.559, and 196.575 respectively for Au. From this conclusion the latter chemists altogether dissent,[2] and express their confidence that in none of the preparations used by them was there free gold sufficient to account for the difference between their own results and those of Krüss.

General Results of Former Determinations most deserving Confidence.

These recent researches, unquestionably by far the most valuable up to the present time, give us, when taken separately and together, the following values for the atomic weight of gold:

1.	General mean of 5 series by Krüss, as calculated by himself	196.640
2.	" " 3 series by Thorpe and Laurie, as calculated by themselves . .	196.852
3.	" " 1 and 2, giving equal value to each,	196.746

Difficulties to be overcome in Determining the Atomic Weight of Gold.

Besides the special difficulties connected with each method which may be adopted, the determination of any high atomic weight with a degree of accuracy which enables the result to be accepted to a given decimal place is clearly a much less easy matter than would be the attainment of an apparently equal degree of precision for an atomic weight represented by a small number. In obtaining the atomic weight of lithium, the first with which, many years ago,

[1] Ber. d. chem. Ges. **20**, 2365. [2] Chem. Soc. Journ., Dec. 1887, p. 868.

I had any personal experience, a difference of unity in the first decimal place corresponded to about $\frac{1}{10}$th of the whole value considered to be correct. In getting the atomic weight of aluminum, worked on later, a like difference represented approximately $\frac{1}{210}$th of the whole value. But, in the case now considered, of the atomic weight of gold, unity in the first decimal place means but about $\frac{1}{1970}$th of the whole value. So that, looking at the matter in this light, it may be said that a degree of precision is demanded more than seven times as great as in the case of aluminum, and twenty-eight times as great as in the case of lithium.

There is also to be noticed, as the most obvious *general* difficulty to which all methods for determining the atomic weight of gold are more or less exposed, the instability of compounds of this metal; not merely the ease with which complete decomposition occurs, with separation of free gold, but the much more insidious and less easily detected trouble arising from the comparative ease with which aurous pass into auric compounds, and the reverse.

New Experiments by the Author.

The general difficulties just alluded to, and the special points to be investigated in regard to each method of determination tried, have demanded much time and work, and I cannot feel even now that all has been done that is desirable and possible; but the experiments projected have been so far completed as to seem to justify publication, and I am not likely soon to be able materially to extend them.

General Principles kept in View.

The improvements made of late years in manipulative methods and apparatus have tended to reduce very much the magnitude of what are commonly called "fortuitous" errors in our quantitative determinations of matter, and to increase greatly the accuracy of such determinations. Probably no modern work has had more influence in this direction than the classic researches of Stas on certain atomic weights—the precautions taken by him, and his remarkable manipulative skill, causing his results to bear almost the same relation to those of his immediate predecessors as did those of Berzelius to the work of the chemists of his earlier day. No one nowadays would undertake the determination of an atomic weight of one of the better known elements without taking such

elaborate precautions as practically ensure pretty close concordance of results, when obtained by the same method, applied in the same hands. In the present state of the question of atomic weights and improvements in their determination, advances in mere delicacy of manipulation and success in merely securing close agreement of results by the same method are not alone sufficient. It cannot be too much insisted upon that we need, besides, well-directed and laborious investigation of possible sources of *constant errors*, and the adoption of means to guard against them. Careful preliminary study is required, in a general way, of the precise nature of each reaction employed, and how it may be influenced by the conditions of the experiment. We learn more and more of late that many of the reactions—perhaps it should rather be said of all the reactions—which have been generally supposed to be of the simplest nature are in reality complex.

The following are among the general principles which seem to be most important, as tending to greater accuracy and trustworthiness in atomic weight determinations; they have been in part stated in the author's earlier paper on the atomic weight of aluminum:

1. In purifying the materials used, both the element of which the atomic weight is to be investigated (or any special compound containing it) and all substances used to react thereupon, resort should in all cases be had to "fractional" methods, assuming materials to be pure only when earlier and later fractions give no signs of any constant difference in the results which they yield.

2. Different and independent processes should be applied to the determination of the same atomic weight, and the results used to check each other. It is desirable that as many such different processes be applied as can be devised, provided each be reasonably free from apparent sources of error, even though it be usually impossible to properly assume that all are equally advantageous in this respect, and therefore of equal value. In the comparison of results obtained it should be noticed whether a given method tends on the whole to yield results probably higher or lower than the truth, though it may be gravely doubted whether the practice is commendable of attempting any numerical estimate of relative value, by so-called "weighting" of the results in calculation.

3. In connection with each process there should be careful study of the reactions depended upon for the final determination

of an atomic weight, looking especially to the possibility of the occurrence of secondary or subsidiary reactions.

4. Each process adopted should be as simple as possible, both in the nature of the chemical reaction or reactions and in the known liability to merely manipulative errors.

5. Each process should be carried out with, in some experiments larger, and in others smaller, quantities of material. But, on the whole, the quantities used should be kept within such limits as are most likely to admit of most accurate determinations being had under the conditions of the special process.

6. In the reactions depended upon only such other elements should be concerned as may be counted among those of which the atomic weights are already known with the nearest approach to exactness.

7. It is particularly desirable that, if possible, the atomic weight to be investigated shall be, by at least one process, compared directly with that of hydrogen, now almost universally taken as the basis for the whole list of the elements. It is remarkable for how very few of the elementary substances—not more than three or four—this direct comparison has been accurately made.

8. In the greater number of the processes available for atomic weight determinations the comparison with hydrogen must perforce be made indirectly. When this is the case, it is desirable that as few other elements as possible, the assumed atomic weights of which will have to be taken into account, shall be involved in each single reaction depended upon.

9. In selecting *different* processes to be applied to the determination of the atomic weight of a given element, in order that the results may check each other, it is desirable that, not the same, but as many different other elements as possible, shall be concerned in the several reactions, provided all such elements count amongst those of which the atomic weights may be considered in the first rank as to the accuracy with which they are known.

Means and Methods of Weighing Employed.

These were in the main the same as those which I had in former years used in determining the atomic weight of aluminum.

The balance chiefly used, made by Becker, was carefully cleaned, and all its parts adjusted, especially as to the position of

the centre of gravity for each load to be used. A second balance by the same maker, of larger size, capable of taking a load of a kilogram in each pan, was employed in weighing certain of the solutions experimented on, and was in like manner carefully adjusted and tested. All weighings were made by observation of the oscillations of the index on either side of the position of rest. A difference of weight of .0001 gram with the smaller balance, and .0002 gram with the larger instrument, was easily and distinctly observable with any load which the research required.

The same kilogram weight was made the basis of a comparison with all my other weights which had been before used in the same way. This had been compared at Washington with the "star kilogram" of the United States Coast Survey, the value of which is known in terms of the original "kilogram of the Archives" at Paris. All the smaller weights were carefully rechecked against this and against each other, and their real values ascertained as referred to a vacuum. The necessary determinations were made of the specific gravity of all materials and vessels which were to be weighed, and the barometer and thermometer were read at the time of each weighing, so that all weights recorded in this paper represent real values *in vacuo*. In order to reduce to a minimum errors due to varying deposition of hygroscopic moisture, vessels of like material, shape and size with those used to contain substances to be weighed were used as tare.

History and Mode of Purification of the Gold used in this Research.

Most of the metal needed was prepared by myself, with precautious presently to be mentioned; a part was obtained, as "proof gold," from the United States Mint at Philadelphia; another part from the United States Assay Office at New York; and a single specimen of English "trial plate" gold from the Royal Mint in London.

1. *Purification of Gold by the Author.*—It may fairly be concluded from the general history of the gold of commerce that the impurities most to be suspected, and most requiring special precautions for their removal, are silver and the metals of the platinum group. My preliminary experiments led me to believe that the greatest difficulty in the way of obtaining perfectly pure gold consists in getting rid of the last traces of silver, the chloride of this metal not being quite insoluble in a solution of auric chloride. For

the removal of silver I have chiefly depended upon evaporation of the gold solution with a little hydrobromic acid, followed by large dilution with water, and long-continued clearing by subsidence. As regards the platinum metals, my results agreed substantially with those of Hoffmann and Krüss,[1] but I have been inclined to lay some stress on reduction of the gold from its solution *with exclusion of light*, and on *fractional* reduction, using only the middle portion thrown down. I avoided altogether the use of ferrous salts as reducing agents, in view of the difficulty of preparing them in large quantity with assurance of their purity and the trouble of thoroughly washing the precipitated gold. For the final precipitation of the gold formic acid seemed to offer real advantages; its volatility admits of easily getting it free from any metallic contamination, and the reduction is more easily effected than with oxalic acid.

Starting with United States gold coin, it was first heated to bright redness in a muffle, as a precaution against the presence of any traces of mercury, and to remove any grease, etc., from the surface, and then dissolved in a mixture of pure hydrochloric and nitric acids in the right proportions. The solution was evaporated with excess of hydrochloric acid nearly to dryness, the auric chloride redissolved in a considerable quantity of water, and the solution allowed to settle for four or five days. The greater part of the clear liquid, drawn off with a syphon, and filtered through very fine siliceous sand,[2] was again evaporated nearly to dryness, adding towards the end a few drops of pure sulphuric acid, in case of the conceivable, though unlikely, presence of such traces of lead as this might reveal; much pure water was added, the solution again cleared by subsidence for several days, and the greater part of the clear liquid again drawn off and filtered. This solution was now rendered pretty strongly acid with hydrochloric acid, and fractionally precipitated by sulphurous acid (SO_2 was evolved from sodium sulphite), at as low a temperature as possible, and *in the dark*, putting aside the first and last portions of the metal thrown down, and reserving for further treatment the (largest) middle portion. The gold thus obtained was well washed with water, boiled with nitric acid alone, again washed, boiled with hydro-

[1] Ann. Chem. (Liebig) **238**, 66.

[2] The sand was carefully purified beforehand by boiling with nitric and hydrochloric acid, thorough washing with water, and heating to redness in the air.

chloric acid alone, again washed, dried, and heated strongly with fused acid sulphate of potassium in a porcelain crucible, boiled with dilute hydrochloric acid, and then with water. The metal was redissolved in aqua regia, the solution evaporated nearly to dryness, with addition of pure hydrobromic acid towards the end, very largely diluted with water, and allowed to stand for two days, well protected from dust, before again syphoning off as much of the clear portion as could be safely removed without risk of disturbing the remainder at the bottom, using a conical precipitating jar with greatest diameter below, and filtering the liquid through siliceous sand as before. The evaporation with hydrobromic acid was repeated twice more, and the clear solution—allowed the last time to stand a month before being syphoned off and filtered—was then reduced, once with oxalic acid (neutralising the liquid with pure sodium hydroxide from the metal), once (after re-solution) with sulphurous acid, and once with formic acid, washing the reduced metal well each time before redissolving in aqua regia. In the first and second of these reductions a little of the metal first and last thrown down was rejected, and in the final reduction with formic acid the first portion precipitated, about one-fifth of the whole, was reserved for use, labelled A, *a*, the middle portion, about three-fifths, was labelled A, *b*, and the last portion, the remaining one-fifth, was also preserved for use, marked A, *c*, so that it might be seen whether any difference in the character of the metal could be detected in the atomic weight determinations. All of these fractions received a very thorough final washing with water.

Such part of the purified metal as was to be used in the preparation of gold compounds was not fused, but was heated in a glazed porcelain tube to moderate redness in a Sprengel vacuum. A small part of the metal used in the free state, and desired in compact form, was fused in a perfectly clean Beaufaye crucible with a little acid sulphate of potassium and borax, the button flattened, boiled with strong nitric and then strong hydrochloric acid, thoroughly washed with water, and, finally, heated in the Sprengel vacuum. Throughout the long process of purification, and especially towards its close, the most scrupulous care was taken to exclude dust, and to prevent grains of sand from the bottoms of beakers or any other impurities getting into the precipitated gold, upon which the acids used would not act, so as to obviate the risk of merely mechanical contamination, which, if

overlooked, might lead to that being weighed as part of the gold which was, in fact, foreign to it.

2. *Purification of "Proof Gold" obtained from the United States Mint at Philadelphia.*—I owed to the kindness of Mr. J. B. Eckfeldt, Chief Assayer to the Philadelphia Mint, a liberal supply of the "proof gold" used in checking the gold assays there made, and he furnished me the following statement of the manner in which this purest metal is prepared, under his directions: "The best cornets from the gold assays selected and dissolved in aqua regia. Solution evaporated, with additions of HCl, to nearly crystallisation, diluted largely with water, and allowed to stand for three or four weeks. About seven-eighths of the solution drawn off from the silver chloride, and passed through several thicknesses of various filters. Solution somewhat concentrated, and alcohol and potassium chloride added, allowed to stand for some time (precip. traces of platinum[1]), and carefully filtered. Gold precipitated by addition of pure ferrous sulphate. Reduced gold washed repeatedly in boiling HCl, until washings show no iron, then well washed in pure water. Gold dissolved, and solution evaporated to crystallisation, with repeated additions of hydrobromic acid,[2] diluted, and again allowed to stand for some time; filtered. Through the solution was passed pure SO_2 until all the gold was reduced; washed. Gold again dissolved, evaporated with HCl, diluted, and oxalic acid added, and heated until all gold is down. Melted in white clay crucible with potassium chlorate and nitrate, afterwards with pure sodium carbonate and borax." Mr. Eckfeldt also informed me verbally that the proof gold thus purified is cast into a small bar in a perfectly clean and bright cast-iron mould; the bar is boiled in nitric acid, washed and dried, rolled between fine steel rolls quite free from grease, and the strip finally cleaned for use with hot hydrochloric and then nitric acid.

In a letter of later date he wrote, "In preparing the 'proof' I seldom make over 10 ounces in one lot; from 8 to 10 ounces is the usual amount. There is comparatively little trouble in making

[1] The platinum of South American native gold, and of scrap gold from dentists, is at the Philadelphia Mint separated solely by alloying with enough silver, and dissolving out the latter metal with nitric acid. The platinum dissolves with the silver.

[2] I had, many months before, independently adopted and used hydrobromic acid to remove traces of silver more effectually than by hydrochloric acid, when I learned from Mr. Eckfeldt that he had thus habitually employed it.

999.9 fine, but beyond that it is rather troublesome; and it seems that, with all the care, the final result is sometimes a little in doubt."

The fine gold received from the Philadelphia Mint is designated as B in this paper, in connection with the experiments in which it was used.

3. *Purification of "Proof Gold" obtained from the United States Assay Office at New York.*—Dr. H. G. Torrey, Chief Assayer in this office, was obliging enough to let me have several samples of his finest proof gold, used in checking the regular assays in his department. He informed me that this proof gold was independently prepared at New York, but was occasionally compared with that of the Philadelphia Mint. He furnished the following brief statement as to its preparation: "The process used in preparing the gold is to dissolve 'cornets' (or gold from assays) in nitro-hydrochloric acid, and after filtration precipitating by oxalic acid, and after thorough washing melting under borax. The operation is conducted with the utmost care throughout."

The gold from this source is designated as C in this paper.

4. *Gold from the "Trial Plate" of Fine Gold of the English Mint.*—Professor Roberts-Austen, Chemist to the Royal Mint, was so kind as to let me have a specimen of a few grams of gold cut from the trial plate of the pure metal prepared by him in 1873. In its preparation use was made of potassium chloride and alcohol to separate any platinum present in the original material, a long period of subsidence was allowed for the deposit of any silver chloride from the solution, and the whole process was applied on a large scale, resulting in the purification of some 70 ounces of fine gold, of which Professor Roberts-Austen himself has said: "I have not been able to prepare, or to obtain from any source, gold of greater purity, even in small quantities." It seems, however, that the apparent standard of this gold was slightly reduced in rolling, the finished plate being counted as 999.95 fine in comparison with the same gold before rolling. A memorandum given me by Professor Roberts-Austen states that this trial plate gold is 999.98 fine as compared with the purest gold obtained by Stas for the Belgian Mint.

This specimen of English trial plate gold is designated as D in the present paper.

All the samples of gold received from others—B, C, and D—

were, before using them, carefully boiled in nitric acid to remove any possible traces of silver or other metal derived from the shears used in cutting the plates. They were also previously well washed with ether, to remove any grease, and afterwards with pure water, and were finally heated to redness in the Sprengel vacuum.

It may be remarked, in advance, that I have not been able to trace any probable connection between the history of the several samples of gold used and the values obtained for the atomic weight of the metal. Within the limits of accuracy attained, the results appear to have been sensibly the same by each method for all the gold used. Nor is there apparent in the results of Krüss, or those of Thorpe and Laurie, any evidence of a difference fairly traceable to the nature of the metal employed by them.

A considerable part of the gold prepared by myself was, after having once served for a determination of the atomic weight, redissolved and reprecipitated, and was afterwards more than once used in subsequent determinations, and yet no sign was obtained of any resulting influence upon the later values of the atomic weight as obtained, evidence being thus furnished of the purity, not only of the gold itself, but of the reagents used to act upon it, so far as any contamination of the metal was concerned. It may therefore be concluded with reason that the gold used in these experiments was of uniform character, and uniformly free from any known impurities, to such an extent, at any rate, as to sensibly change the results obtained.

It is to be noted that the only known elements having higher atomic weights than that of gold are mercury, thallium, lead, bismuth, thorium, and uranium. The presence of any of these in the gold experimented on, even in traces too minute to weigh, is in a very high degree unlikely. The presence of any other element or elements than these would, for analogous compounds, tend to lower the value obtained for the atomic weight of gold; so that, in considering the chances of error due to the nature of the metal used as gold, we should be inclined to say that the risk was rather in the direction of too low than too high a result being reached. But, if the possibility be observed of compounds not analogous being erroneously compared, the contrary error will be seen to be possible. Thus, in case the composition of an auric haloid salt obtained from a given amount of metallic gold should be examined, if any unsuspected silver were present there would be required for

the same amount of the halogen three atoms of silver instead of one atom of gold, and, therefore, the apparent weight of gold as compared with that of the halogen would be increased instead of diminished, and a higher value obtained for the atomic weight sought.

General Precautions Observed in the Experiments for Determination of the Atomic Weight.

All the reagents used were prepared or purified by myself, and most carefully tested for any traces of such impurities as might reasonably be suspected, and as could affect their application to the purpose in view. Particular care was bestowed upon the examination of the distilled water, acids, and other materials used in large quantity. To remove organic matter from the water required, it was distilled from a small amount of potassium permanganate and sulphuric acid.

Scrupulous care to exclude atmospheric dust was observed. In the evaporation of some of the gold solutions the process was carried out in a glass bottle of considerably larger capacity than the volume of liquid to be treated, furnished with a well-ground glass stopper of special construction, as shown in figs. 1 and 2, the

FIG. 1.

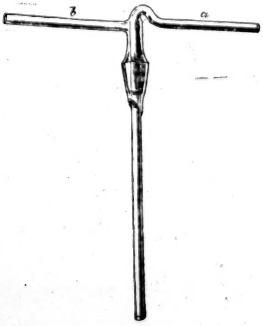


FIG. 2.

latter representing the stopper in place. Air, purified by passing through a red-hot tube, then through a solution of potassium permanganate and sulphuric acid, and dried by passing through

concentrated sulphuric acid and over solid potash, was introduced by the tube *a*, which went down to near the level of the liquid to be evaporated, while this air, charged with vapor of water from the liquid, was withdrawn through the tube *b* by means of a water-jet pump; the bottle was moderately heated by immersion to the greater part of its height in a water-bath.

In filtering the gold solutions no paper or other organic material was used, but fine white siliceous sand, previously boiled in nitric and hydrochloric acids, washed with water, and well ignited to burn off any organic matter, was substituted, supporting it on coarser sand and larger fragments of quartz, similarly purified, and the whole arranged so as to prevent the possibility of any sand grains being mechanically carried into the filtered liquid. Vessels of hard glass and Berlin porcelain were employed. Care was taken to work in a clean laboratory atmosphere, free from gases or vapors which might affect the materials dealt with.

First Series of Experiments.

A neutral solution of auric chloride was prepared by cautiously heating auric chloride, made, as suggested by Julius Thomsen, by the direct action of pure chlorine upon finely divided metallic gold, until such an amount of chlorine had been given off that on treating the residual material with moderately warm water, metallic gold only remained undissolved, which was then filtered off. This neutral solution having been rendered uniform by agitation, two approximately equal portions of it were weighed off, using, of course, stoppered vessels to prevent evaporation during the weighing. From one of these portions the gold was thrown down in the metallic state by pure sulphurous acid with the aid of heat, carefully collected, well washed, dried, ignited in a Sprengel vacuum, and weighed. To the other portion there was added the carefully prepared solution in a minimum of nitric acid of an accurately weighed quantity of pure silver, a little more than equivalent to the chlorine present, the liquid and precipitate digested together for a considerable time with gentle warming in a stoppered glass flask, well agitated from time to time, and the precipitate (of silver chloride, containing also the gold) filtered off upon siliceous sand, and thoroughly washed, avoiding throughout the decomposing influence of light. The clear filtrate was nearly neutralised with pure sodium hydroxide (from metallic sodium),

evaporated down to a small bulk, using the vessel represented in fig. 2 (p. 91), and finally the remaining silver was determined (with all the needful precautions of the silver assay) by means of a weighed quantity of a weak solution of pure hydrobromic acid standardised against pure silver. This mode of determining chlorine by means of silver and hydrobromic acid was suggested to me in a letter, of the 27th of January, 1887, with which I was favored by M. Stas,[1] who advocates it as the most exact process available. The pure silver required was prepared in the same way as that used in my experiments on the atomic weight of aluminum,[2] and was heated in the Sprengel vacuum to remove all occluded gas. The hydrobromic acid was prepared as directed by Stas in his published paper—"De la détermination du rapport proportionnel entre l'argent, les chlorures et les bromures."[3]

In reporting the results obtained, the quantity of gold stated is that actually weighed, but the quantity of silver corresponding thereto has, for the sake of simplicity, been given as that required for an exactly equal quantity of the auric chloride solution, while, as stated above, the quantity of liquid weighed off was very nearly, but not exactly, equal to that from which the gold was thrown down, the difference being allowed for in calculation.

With this explanation the results of the first series of experiments were as follows:

Experiment.	Character of gold used.	Gold, grams.	Silver required to precipitate Cl, grams.
I.	A, *a*	7.6075	12.4875
II.	A, *b*	8.4212	13.8280
III.	B	6.9407	11.3973
IV.	A, *c*	3.3682	5.5286
V.	C	2.8244	4.6371

In regard to conceivable sources of error connected with this method, it is to be observed that, in preparing the original auric chloride solution, if there should be any reaction between this gold salt and the water, leading to the formation of traces of hydrogen

[1] In this letter M. Stas says, "Je me permets de vous recommander l'emploi de l'acide bromhydrique pour la précipitation de l'argent resté dans un liquide après une double décomposition opérée à l'aide d'un *chlorure* et d'un sel d'argent. On réussit à condition que l'eau mère renferme un excès d'argent dont le poids est le triple du metal qui peut rester en solution à l'état de chlorure d'argent."

[2] Phil. Trans. 1880, p. 1020.

[3] Mémoires de l'Acad. Royale des Sciences de Belgique, 43 (1882).

auri-chloride and precipitation of a little auric oxide or hydroxide, which might escape observation in admixture with the metallic gold left undissolved, the tendency would be to lower the atomic weight found for gold. If, by reaction between this residual metallic gold and the auric chloride solution, any traces of aurous chloride were produced and taken up by the solution of the higher chloride, the effect would be to raise the apparent value of the atomic weight.[1]

If, in the reaction of the silver solution upon that of auric chloride, *partial* withdrawal of chlorine should lead to the formation of any traces of aurous chloride, precipitated along with the chloride of silver, and not afterwards decomposed during the digestion of the precipitate with the remaining solution, the resulting error would also be in the direction of too high an atomic weight. The probability of the last supposition is diminished by an excess of silver for the whole amount of chlorine present having been added at once. It is not very likely that any one of these defects actually belongs to the method and affects its results to a sensible extent. Of the three I should be more inclined to suspect the possibility of the second than either of the two others.

Second Series of Experiments.

A neutral solution of auric bromide was prepared by a like process to that used in making the auric chloride of the first series: acting upon pure metallic gold with pure bromine (prepared with the precautions recommended by Stas), evaporating the solution to dryness out of reach of dust, cautious heating of the residue, re-solution of auric bromide, and filtration from undissolved metallic gold.

Two nearly equal portions of the solution were accurately weighed off, and treated as described above: in one reducing the gold to the metallic state and determining its weight; treating the other with a small excess of silver in solution as nitrate, filtering off the precipitate, concentrating the filtrate with the precautions already described, and determining in it the excess of silver by means of hydrobromic acid.

Reducing the amounts of silver actually used to the corresponding quantities for portions of auric bromide solution exactly

[1] These two remarks apply, of course, also to Krüss's first series of experiments.

equal to those from which in each case the gold was obtained, the results in six experiments stood as follows:

Experiment.	Character of gold used.	Gold, grams.	Silver required to precipitate Br, grams.
I.	A, *b*	8.2345	13.5149
II.	A, *c*	7.6901	12.6251
III.	B	10.5233	17.2666
IV.	A, *a*	2.7498	4.5141
V.	C	3.5620	5.8471
VI.	A, *b*	3.9081	6.4129

In these experiments the sources of constant errors which suggest themselves as possible are essentially similar to those for the first series; but, if any such really exist, there is, of course, the likelihood of some difference being introduced by the substitution of bromine for chlorine. Hence the desirability of multiplying experiments in this modified form.

Third Series of Experiments.

For these experiments potassium auri-bromide was prepared with great care from an excess of metallic gold treated with bromine and potassium bromide, purified in accordance with Stas's suggestions, and the double salt five times recrystallised. The last crystallisation was conducted fractionally, in closed vessels, with special care to exclude dust, by gradual but pretty rapid cooling with agitation, and the earlier and later portions separated out were kept apart in after use.

For each atomic weight determination an unweighed quantity of this potassium auri-bromide was dissolved in water, the solution rendered uniform by agitation, and divided into two nearly equal parts, which were severally weighed with accuracy, and in one the gold reduced to metal as in the experiments of the first and second series, and in the other the total bromine precipitated by silver solution as before, the comparison being made once more between the weight of the gold and that of the silver equivalent to the bromine (in this case representing 4 atoms) existing in the double bromide.

Again stating the quantities of silver corresponding to portions of the auri-bromide solution exactly equal to those used in determining the gold, the following were the results obtained:

Experiment.	Character of gold used.	Fraction of crystallised auri-bromide used.	Gold, grams.	Silver required to precipitate Br, grams.
I.	A, *b*	First	5.7048	12.4851
II.	A, *b*	Second	7.9612	17.4193
III.	B	First	2.4455	5.3513
IV.	B	Second	4.1632	9.1153

Of the tendencies to constant error which may be imagined in connection with the experiments of the first two series, and which have been noticed above, the first may probably be considered as not applying to the method pursued in this third series, while the second and third might still be applicable. But the superior stability of the double salt constitutes an advantage in its favor, and, as it formed the chief material for the experiments of Krüss and of Thorpe and Laurie, a comparison with their results is desirable, the mode of treatment pursued by me in ascertaining the composition of the salt not having been quite the same as that used by these chemists.

Fourth Series of Experiments.

A weighed quantity of trimethyl-ammonium auri-chloride, $[N(CH_3)_3HAuCl_4]$, was decomposed by heating in the air, and the weight of the residual metallic gold determined. This trimethylamine salt was selected because the base is of simple and well established constitution, and may with reasonable probability be counted upon as obtainable in a state closely approaching purity, and because the gold salt is easily crystallised, possesses a considerable degree of stability, and contains approximately half its weight of gold, so as to offer the most favorable chance of determining with accuracy the ratio between the metal left behind and the sum of the remaining constituents driven off on ignition. Although its use in fixing the atomic weight of gold involves the atomic weights of three other elements—carbon, nitrogen, and chlorine—all three of these constants deserve to be ranked amongst those already known with the nearest approach to precision at present attainable.

In order to obtain pure trimethyl-ammonium chloride, the impure commercial salt, derived from the *vinasse* of beet-root sugar making, was used, first setting free and distilling off a considerable quantity of trimethylamine and condensing at about the right temperature, and subsequently purifying the product by

Hofmann's method of treatment with ethyl oxalate and renewed distillation. The purified trimethylamine was several times fractionally distilled, and the portion of correct and most constant boiling point finally neutralised with pure hydrochloric acid. The concentrated solution of trimethyl-ammonium chloride was now precipitated by a strong solution of auric chloride, the mother liquor decanted off, and the gold salt redissolved in hot water, and recrystallised several times. The bright yellow crystalline powder was dried, first over sulphuric acid and afterwards over phosphorus pentoxide, until it ceased to lose weight; towards the end of the drying the temperature of the vessel was raised to about 50° C. Preliminary experiments seemed to indicate the probable existence of this salt crystallised with a single molecule of water, but most of that prepared contained no constituent water, and it appeared easy to attain complete drying without any decomposition of the salt itself. Throughout its treatment the salt, which was not in any high degree hygroscopic, was well guarded from dust and from any possible decomposing effect of light.

The portion of the salt to be used in each experiment was contained in a small glass-stoppered weighing flask, which was removed just before it was needed from the phosphorus pentoxide desiccator, the stopper having been inserted; the flask was weighed, the greater part of its contents transferred quickly to a weighed porcelain crucible, the stopper at once replaced, and, the flask being again weighed, the quantity of gold salt taken from it was found by difference.

In order to avoid mechanical loss by spattering on igniting the crucible and its contents, the auri-chloride lying together at the bottom of the crucible was covered by a layer, nearly a centimetre deep, of clean, carefully purified, and just previously well-ignited siliceous sand, the weight of this sand being known by taking it from a weighing flask in which it had been cooled over phosphorus pentoxide, and noting the loss of weight of this flask. In applying heat to the crucible and its contents it was found necessary to heat gently for a long time, raising the temperature slowly, in order to prevent extensive charring at the bottom. Then, before the temperature had become too high, but after a considerable part of the volatile matter had been driven off, the sand was carefully stirred in with the remaining material so as to produce pretty

uniform mixture, in order that the gold might not undergo partial welding together at a high temperature, which might have led to wrapping up particles of carbon and their protection from combustion. In this operation a very small porcelain stirrer was used, as a platinum wire would have welded on and taken up some of the metallic gold; the weight of this stirrer was determined in advance, and checked after use. Finally, the contents of the crucible were submitted to very careful and prolonged heating to moderate redness, with free access of air and occasional cautious stirring, so as to burn away every trace of carbon. After cooling in a desiccator, the crucible and its remaining contents were weighed, giving the weight of the residual gold by subtraction of the weights of the crucible itself and the siliceous sand. As an additional safeguard against any particles of carbon left unburned escaping detection, the gold was afterwards dissolved out with aqua regia, and the white sand carefully looked over with a lens.

The results of five experiments thus conducted were as follows:

Experiment.	Character of gold used.	Character of gold salt used.	Salt ignited, grams.	Residual gold, grams.	Loss by ignition, grams.
I.	A, *b*	Earlier crop of crystals	14.9072	— 7.3754	= 7.5318
II.	A, *b*	Middle " " "	15.5263	— 7.6831	= 7.8432
III.	A, *b*	Last " " "	10.4523	— 5.1712	= 5.2811
IV.	C	Middle " " "	6.5912	— 3.2603	= 3.3309
V.	C	Last " " "	5.5744	— 2.7579	= 2.8165

In these experiments the most probable source of error may be fairly taken as arising from the presence of traces of methyl-ammonium or dimethyl-ammonium auri-chloride with the trimethyl-ammonium salt. I know of no direct evidence that any such impurity was present, and the absence of any such evidence in the results from the earlier as compared with the later crops of crystals rather tells against the supposition of its presence, but one cannot feel certain of its entire absence. If present, its effect would be to raise the atomic weight obtained for gold. It is also conceivable that there may have occurred volatilisation of gold to a minute extent as auric chloride, in accordance with the observation of Krüss that this salt may be sublimed in small quantity at moderate temperatures in a stream of chlorine; but, there being no such stream of chlorine in these experiments, and on the contrary the decomposing action of the hydrogen of the trimethylamine salt, this does not seem likely; the effect would, of course, be to

raise the atomic weight obtained for gold. Another possible cause of error might consist in imperfect drying of the gold salt used, but the constancy of weight attained on drying renders it unlikely that any other than extremely minute error should come of this, though not altogether excluding the possibility of its occurrence; its tendency would, of course, be to lower the atomic weight obtained. Any trouble from hygroscopic moisture on the surface of the porcelain crucible and sand was, I think, satisfactorily guarded against by the use of a corresponding tare crucible, and by more than one weighing after a near approach to the true values had been obtained, the crucibles having meanwhile been restored to the desiccator and kept therein for some time. The precautions taken seemed to afford sufficient protection against any merely mechanical loss during the ignition.

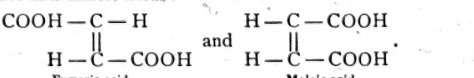
[*To be continued.*]

ON THE SYNTHESIS OF FUMARIC ACID.

(*Preliminary Communication.*)

By E. H. Keiser.

Van't Hoff[1] has proposed the following stereometric formulas for fumaric and maleic acids:



Fumaric acid. Maleic acid.

Johannes Wislicenus[2] has shown in a series of important papers that it is possible to determine experimentally the stereometric formulas of certain isomeric compounds. A consideration of the hypothesis put forward by him suggested the idea that it ought to be possible to prepare both fumaric and maleic acids synthetically from acetylene. In accordance with Van't Hoff and Wisli-

[1] Lagerung der Atome im Raume, p. 21.

[2] Räumliche Anordnung der Atome in organischen Molekulen. Ann. Chem. (Liebig) **246**, 53.

cenus's theory, the di-halogen additive compounds of acetylene can exist in two isomeric forms having the formulas

$$\text{I.}\quad \begin{matrix} X-C-H \\ \| \\ H-C-X \end{matrix} \quad \text{and} \quad \text{II.}\quad \begin{matrix} H-C-X \\ \| \\ H-C-X \end{matrix},$$

in which X represents any halogen atom. And further, compounds having the constitution represented by formula I are more stable than those having the structure represented by the second formula. Fumaric acid would then appear to be closely related to the halogen derivatives of the first class and maleic acid to those of the second.

It occurred to me that it might perhaps be of interest in this connection to start with acetylene and prepare, in the first place, two isomeric di-halogen additive compounds, and then endeavor to transform these into fumaric and maleic acid. The investigation is not yet completed, but one of the acids—namely, fumaric acid—has been prepared in this way from acetylene.

Acetylene was prepared by the action of alcoholic potash upon ethylene bromide, and the purified gas was passed through a series of wash bottles containing crystals of iodine covered with a layer of absolute alcohol. After a time the iodine disappeared, and from the liquid two isomeric acetylene diiodides were separated. One of these compounds is a solid at ordinary temperatures, the other is a liquid. The solid diiodide is much more stable than the liquid variety. It does not decompose on standing, and can be sublimed without suffering change. On the other hand, the liquid diiodide undergoes decomposition when heated, and cannot be distilled with steam without being decomposed. These compounds have been prepared by Sabanejeff,[1] who has analysed them, and found them to have the composition represented by the formula $C_2H_2I_2$. No attempt was made by him to determine their constitution.

In accordance with the Van't Hoff hypothesis, the solid acetylene diiodide, which is much more stable than the liquid diiodide, would have the constitution represented by the formula $\begin{matrix} I-C-H \\ \| \\ H-C-I \end{matrix}$ and would, therefore, belong to the same general class of acetylene derivatives to which fumaric acid belongs. Now, experiment shows that this solid acetylene diiodide can be transformed into fumaric acid.

[1] Ann. Chem. (Liebig) **178**, 118.

Nine grams of the acetylene diiodide crystals (m. p. 73°) were dissolved in alcohol, and 5 grams (2 molecules) of potassium cyanide added, and the solution was boiled for 36 hours in a flask with an inverted condenser. Caustic potash was thereupon added, and the boiling continued for two hours longer. On cooling the contents of the flask, a considerable quantity of needle-shaped crystals separated from the liquid. They were removed from the solution, and on examination proved to be the potassium salt of fumaric acid, which crystallises in the form of needles, insoluble in cold alcohol. More of the salt was obtained from the mother-liquor. The aqueous solution of the potassium salt was treated with silver nitrate, and a white precipitate consisting of the silver salt was obtained. The silver salt was purified by dissolving it in nitric acid and reprecipitating it by carefully neutralising the solution with ammonia. The silver salt of fumaric acid is characterised by its great insolubility in water and by the fact that when it is heated it deflagrates like gunpowder. Both of these properties were exhibited by the silver salt of the acid made by synthesis.

A quantitative determination of the percentage of silver gave the following result:

.2039 gram of the salt dried at 100° gave .1786 gram of AgCl = 65.97 per cent. Ag.

	Calculated for $Ag_2C_4H_2O_4$.	Found.
Ag	65.43	65.97

The free acid itself was recognised by its insolubility in water: it was precipitated from moderately concentrated solutions of its salt by the addition of strong acids. It will be analysed as soon as larger quantities of it have been obtained in pure condition.

In 1882 Sabanejeff[1] studied the action of potassium cyanide upon acetylene dibromide and obtained an acid having the formula $C_4H_6O_5$. It is probable that fumaric or maleic acid was first formed in his experiments, which afterwards, by the prolonged action of boiling caustic alkali, was converted into the acid $C_4H_6O_5$. It has been shown by Linnemann and Loydl[2] that when fumaric acid is heated with caustic alkalies it is gradually changed into an inactive maleic acid, thus:

$$\underset{\text{Fumaric acid.}}{C_4H_4O_4} + H_2O = \underset{\text{Inactive maleic acid.}}{C_4H_6O_5}.$$

[1] Ann. Chem. (Liebig) **216**, 275. [2] Ann. Chem. (Liebig) **192**, 80.

A more detailed study of the reactions which give rise to the formation of the two acetylene diiodides, as well as the attempt to prepare maleic acid from acetylene, is reserved for future work.

BRYN MAWR, PA., *February*, 1890.

A METHOD FOR THE DETECTION AND ESTIMATION OF PETROLEUM IN OIL OF TURPENTINE.

BY W. M. BURTON.

The use of the lighter boiling products of petroleum for the purpose of adulterating oil of turpentine is so well known to persons using these articles that little comment is necessary concerning the prevalence of this adulteration. Refined petroleum of the proper color and gravity can be mixed with turpentine in such proportions as to elude the common methods of detection. The gravity, color and odor of the mixture can be made identical with that of turpentine; whereas paint made from such material is not durable, but is liable to crack and peel off soon after its application. The pecuniary advantage to the unscrupulous dealer is also a great temptation to perpetrate this adulteration on the large scale. Allen, in his "Commercial Organic Analysis" (Vol. II, p. 441), describes a method for the detection of petroleum in turpentine. According to his description, the mixture is treated with strong sulphuric acid, when the terpenes are converted into polymers of a tarry consistency, while the petroleum is very slightly affected. This mixture is placed in a flask and steam blown through the mass, when a portion of the petroleum will be volatilised and can be collected in the usual way. This method requires considerable time and labor to obtain fair results, and, further, the yield of petroleum is far from being quantitative, leaving the operator in the dark as to the extent of the adulteration. The method which is here proposed is based upon the fact that petroleum is only slightly affected by fuming nitric acid in the cold, whereas turpentine is readily oxidised to various acids of the fatty and aromatic series, which are soluble in hot water. If, therefore, we treat a mixture of turpentine and refined petroleum with

cold fuming nitric acid, the terpenes will all be converted into acids readily soluble in hot water, while the paraffins of the petroleum will remain almost entirely unaffected. These facts enable us to determine almost quantitatively the amount of petroleum contained in adulterated turpentine. The apparatus necessary for effecting this separation is very simple. A balloon flask of 750 cc. capacity is fitted with a two-hole cork stopper. Through one hole is inserted the tube of a glass-stoppered drop funnel having a capacity of 100 cc. The flask is also connected with an inverted condenser. About 300 cc. fuming nitric acid of sp. gr. 1.4 are placed in the flask, and 100 cc. of the turpentine to be tested are measured into the drop funnel. The flask is surrounded by cold water, and the turpentine is allowed to drop slowly into the nitric acid. As each drop strikes the acid, violent action takes place, with evolution of red fumes. It is well to shake the flask occasionally during the operation. When the turpentine has all passed into the flask, the apparatus is allowed to stand until all action is over. The contents of the flask are transferred to a large separating funnel and treated with successive portions of hot water. In this way all the products resulting from the action of the acid on the terpenes are removed, while any petroleum paraffins remain insoluble in water, and can readily be separated and measured.

Having procured some turpentine known to be free from petroleum, my assistant prepared mixtures of the pure turpentine with samples of refined petroleum of various boiling points. In order that my judgment in experimenting might not be influenced by knowing the quantities of material used, my assistant withheld from me the proportions employed in the mixtures. Ten mixtures were analysed, with the following results:

Pure turpentine used.	Petroleum used.	Boiling point of petroleum.	Petroleum found by method described.
65 cc.	35 cc.	about 250°	34.1 cc.
80	20	250	18.9
70	30	200	29.
80	20	200	18.5
90	10	200	8.9
80	20	100	17.8
70	30	100	28.4
85	15	100	13.5
80	20	75	17.9
70	30	75	28.

It will be noticed that the sum of the amounts of petroleum and turpentine used would be 100 cc. in each case, so that the number of cubic centimeters of petroleum found would also express the percentage of adulterant. It appears from the above results that the petroleum fractions which boil at about 250° are least affected by the fuming nitric acid, while the low-boiling fractions are affected the most. But in order to keep the specific gravity of the turpentine where it should be, the higher boiling petroleum fractions must be used in the adulteration—a fact which is favorable for the application of this method in the analysis of such mixtures.

CLEVELAND, OHIO, *December*, 1889.

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND LEE K. FRANKEL.

The study of the electrolysis of the double cyanides of cadmium, copper and zinc enabled us to formulate conditions by which the separations of cadmium from zinc,[1] and cadmium from copper,[2] were possible, and in every particular satisfactory.

The ease with which cadmium was separated from zinc, and the very close results obtained with these metals, led us to apply the method to the separation of cadmium from cobalt and from nickel. Operating first with cadmium alone, we dissolved sufficient pure sulphate in water, so that 10 cc. of the solution would contain 0.1688 gram metallic cadmium. To this volume (10 cc.) were added four and one-half grams pure potassium cyanide, and the solution made up to 200 cc. with water. A current yielding 0.4 cc. OH gas per minute was allowed to act upon the same for a period of fourteen hours.

The deposited metal weighed 0.1686 gram, a difference of —0.11 per cent. from the theoretical. A second trial, with conditions precisely analogous to those just mentioned, gave 0.1690 gram cadmium, a difference of + 0.11 per cent. from the theoretical.

[1] This Journal **11**, 352. [2] J. Anal. Chem. **3**, 385.

Cadmium from Cobalt.

In the third experiment the conditions were the same as before, with this difference, that an equal amount of cobalt was also present in the solution. The result of the electrolysis gave 0.1689 gram cadmium, a difference of +.05 per cent. from the required.

The fourth experiment, similar in every way to the third, yielded 0.1689 gram cadmium, a difference of +.05 per cent. from the theoretical.

The cadmium was fully deposited on both occasions, and contained no cobalt.

Cadmium from Nickel.

Passing to the separation of cadmium from nickel, the results were so surprising that we give the same in detail, although negative in character:

	Cadmium present, in grams.	Nickel present.	Potassium cyanide, in grams.	Total dilution.	Strength of current in cc. OH gas per minute.	Cadmium found.
(1)	0.1688	100 per cent.	4½	200 cc.	0.3 cc.	0.1717
(2)	"	"	"	"	"	0.1702
(3)	"	"	"	"	"	0.1725
(4)	"	"	"	"	"	0.1750
(5)	"	"	"	"	"	0.1721
(6)	"	"	"	"	"	0.1737
(7)	0.1828	—	"	"	0.5	0.1827
(8)	"	75	"	"	"	0.1923
(9)	"	50	"	"	0.15	0.1841
(10)	"	"	"	"	0.5	0.1882
(11)	"	25	"	"	0.15	0.1854

The period of time during which the current acted in each of the above experiments was sixteen hours. Nickel was always found in the cadmium deposit, while in many cases the precipitation of the cadmium was incomplete. The conditions were varied, yet the results were wholly unsatisfactory. By greatly increasing the quantity of cyanide, we discovered that the cadmium precipitation was greatly retarded. Nickel, when alone and under the conditions given above, would not deposit with the strength of current used by us. This behavior is only another indication that if we would make electrolytic methods widely applicable, it is first necessary to extend the study of the action of the current to all

the salts possible, and investigate carefully the influence of each metal upon its associates under varying conditions.

From what we have thus far accomplished we find the electrolytic separation of cadmium from copper, from zinc, and from cobalt, in cyanide solution, all that could be expected from any method.

The cadmium deposits, in the experiments recorded in this paper, were always washed with boiling water; the drying was done upon the edge of a warm iron plate.

We have already called attention[1] to the fact that mercury is fully precipitated from its double cyanide by a comparatively feeble current, and that the separation of this metal from copper is possible so long as the quantity of the latter does not exceed 20 per cent. of the mercury present. More recently we have executed a series of experiments looking to the separation of mercury from zinc, nickel, and cobalt.

Mercury from Zinc.

The results with these metals are:

	Mercury present, in grams.	Zinc present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in per cent. from theoretical.
(1)	0.1715	—	4½	200 cc.	0.3 cc.	0.1717	+ 0.12 %
(2)	0.1715	—	"	"	"	0.1715	...
(3)	0.1715	100 %	"	"	0.25	0.1706	— 0.52
(4)	0.1715	"	"	"	"	0.1709	— 0.34

The time in each deposition was sixteen hours. From these figures the separation is possible. Mercury was not found with the zinc. In the following experiments it will be observed that the error is much less, and accordingly makes the method trustworthy and, from its accuracy, well suited for scientific as well as technical work:

	Mercury present, in grams.	Zinc present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in per cent. from theoretical.
(5)	0.2440	100 %	3	200 cc.	0.5 cc.	0.2435	— 0.20 %
(6)	"	"	3	"	"	0.2445	+ 0.20
(7)	"	"	4½	"	"	0.2441	+ 0.04
(8)	"	"	"	"	0.28	0.2445	+ 0.20
(9)	"	"	"	"	"	0.2431	+ 0.37
(10)	"	"	"	"	"	0.2454	+ 0.50

[1] This Journal **11**, 264.

The time of precipitation, made at the ordinary temperature, amounted to sixteen hours. The mercury deposit was washed with hot water and dried upon a moderately warm plate.

Mercury from Nickel.

With these two metals the current was allowed to act for sixteen hours. The results are:

	Mercury present, in grams.	Nickel present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in per cent. from the theoretical.
(1)	0.2440	100 %	4½	200 cc.	0.4 cc.	0.2435	— 0.20 %
(2)	"	"	"	"	"	0.2432	— 0.32
(3)	"	"	"	"	"	0.2425	— 0.60

Mercury from Cobalt.

Our experience with these two metals was so unexpected that we append the poor as well as the good results, which were finally obtained:

	Mercury present, in grams.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Mercury found.	Difference in per-centage.
(1)	0.2440	100 %	4½	200 cc.	0.4 cc.	0.2386	— 2.21 %
(2)	"	"	"	"	0.4	0.2388	— 2.13
(3)	"	"	"	"	"	0.2364	— 3.11
(4)	"	"	"	"	"	0.2333	— 4.00
(5)	"	"	"	"	"	0.2366	— 3.02

The current acted for sixteen hours. Upon reducing the quantity of cobalt, and operating with the conditions in other respects the same as before (except in 11 and 13), we obtained:

	Mercury present.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Mercury found.	Difference in per-centage.
(6)	0.2440	75 %	4½	200 cc.	0.5 cc.	0.2353	— 3.56 %
(7)	"	"	"	"	0.86	0.2357	— 3.40
(8)	"	50	"	"	0.50	0.2385	— 2.25
(9)	"	"	"	"	"	0.2381	— 2.33
(10)	"	"	"	"	0.86	0.2321	— 4.80
11)	"	25	3	"	0.5	0.2442	+ 0.09
(12)	"	"	4½	"	0.86	0.2342	— 4.01
(13)	"	12½	3	"	0.5	0.2445	+ 0.20

Inspection of these figures discloses the fact that nothing

approaching a separation of the two metals appears probable until in Experiment 11, where not only the quantity of cobalt is reduced, but also that of the potassium cyanide. The result is then surprisingly close (+ .09 per cent.). This would seem rather to be due to the reduction of the quantity of cyanide, inasmuch as by its increase in Experiment 12 we again have a minus error of 4.01 per cent., and in Experiment 13, by reducing the quantity of cyanide to 3 grams, the result is satisfactory. As the quantity of cobalt in this instance was but half that in Experiment 12, the favorable result might be attributed to this, hence the following trials were made:

	Mercury present.	Cobalt present.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Mercury found.	Time of precipitation.	Difference in percentage.
(14)	0.2250	—	3	200 cc.	0.5 cc	0.2250	16 hours.	—
(15)	"	25 %	"	"	"	0.2256	"	+ 0.26%
(16)	"	50	"	"	"	0.2258	"	+ 0.35
(17)	"	75	"	"	"	0.2258	"	+ 0.35
(18)	"	100	2.2	"	"	0.2235	"	— 0.60

Cobalt was not found in the mercury deposit, nor mercury in the cobalt solution. Evidently the quantity of cyanide present exercises a marked influence upon the separation. Returning to the separation of cadmium from cobalt, it will be observed that there the amount of cyanide was 4½ grams, while the quantity of metal was less, yet the separation proved satisfactory.

Silver from Copper.

It yet remains for us to record some experiments upon the separation of these two metals in cyanide solution. Reference to a former paper[1] will show that our attempts in this direction were at that time fruitless. It was after the successful separation of cadmium from copper in cyanide solution that we were impressed with the idea that the separation of silver from copper ought to occur, since silver deposits so readily, even when exposed to a very feeble current. In the communication to which we refer the current strength recorded was 1 cc. OH gas per minute. Since it was by carefully reducing this in other cases that we obtained good separations, we instituted a new series of experiments with silver and copper, acting upon the mixture with a much weaker current:

[1] This Journal **11**, 264, and J. Anal. Chem. **3**, 254.

	Silver present, in grams.	Copper present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Time in hours.	Silver found.	Difference in per-centage.
(1)	0.1788	—	4½	200 cc.	0.10 cc.	16	0.1792	+ 0.22 %
(2)	"	—	"	"	0.23	"	0.1788	...
(3)	"	100 %	"	"	0.15	"	0.1788	...
(4)	"	"	"	"	0.30	"	0.1787	— 0.05
(5)	"	"	"	"	0.20	"	0.1784	— 0.20
(6)	"	"	"	"	"	"	0.1782	— 0.33
(7)	"	"	"	"	0.40	"	0.1783	— 0.28
(8)	"	"	"	"	0.15	"	0.1800	+ 0.60

We next dissolved 0.1732 gram pure metallic silver; to its solution were added 100 per cent. copper and 4½ grams KCN. On electrolysing with a current of 0.15 cc. OH gas per minute, the resulting silver weighed 0.1725 gram. The latter contained no copper, nor could silver be detected in the copper solution.

A silver coin (ten cent piece) weighing 1.2236 gram was brought into solution and diluted to 100 cc. Of this solution two portions (25 cc. each) were electrolysed in the presence of 4½ grams KCN, with a current of 0.4 cc. OH gas per minute. The silver found was in

a. 89.64 per cent. *b.* 89.56 per cent.

Two silver determinations made with another coin gave

c. 89.44 per cent. *d.* 89.44 per cent.

A silver dime weighing 2.4507 grams—carefully cleaned with sodium hydroxide and alcohol—after solution in nitric acid and the expulsion of the excess of the latter, was electrolysed with a current of 0.7 cc. OH gas per minute in the presence of 7 grams KCN, and gave 2.1996 grams Ag = 89.79 per cent.

So far as we are aware this is the first electrolytic method which has been proposed for the separation of these metals.

Silver from Zinc.

No difficulty is experienced in separating these metals when in cyanide solution. Our results are as follows:

	Silver present, in grams.	Zinc present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Time in hours.	Silver found.	Difference in per-centage.
(1)	0.1788	100%	4½	200 cc.	0.23 cc.	16	0.1784	— 0.22 %
(2)	0.1788	"	"	"	0.40	"	0.1785	— 0.11
(3)	"	"	"	"	0.4	"	0.1779	— 0.50
(4)	"	"	"	"	0.4	"	0.1787	— 0.05

Applying the same procedure to the separation of

Silver from Nickel,

the results were good:

	Silver present, in grams.	Nickel present.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Time in hours.	Silver found.	Difference in percentage from theoretical.
(1)	0.1788	100%	4½	200 cc.	0.35 cc.	16	0.1785	— 0.16%
(2)	"	"	"	"	"	"	0.1778	— 0.50

Silver from Cobalt.

	Silver present, in grams.	Cobalt present.	KCN in grams.	Total dilution.	Strength of current in cc. OH gas per minute.	Time in hours.	Silver found.	Difference in percentage
(1)	0.1788	100%	4½	200 cc.	0.35 cc.	16	0.1728	...
(2)	0.1788	"	"	"	"	"	0.1747	...
(3)	0.1788	"	"	"	"	"	0.1758	...
(4)	"	"	"	"	"	"	0.1697	...

Recalling our experience in separating mercury from cobalt, we reduced the quantity of cyanide to three grams, and obtained:

(5)	0.1788	"	"	"	"	"	0.1794	+ 0.33%
(6)	"	"	"	"	"	"	0.1782	— 0.33

From experiments made to learn the action of the current upon solutions of cobalt in the presence of a great excess of potassium cyanide, we know that the higher cyanide of cobalt—the cobalticyanide—is produced, and may it not be this which in some manner combines with the last traces of mercury and silver to form double cyanides not decomposable by the current strength employed in our experiments, which, if increased, would not only throw out the mercury and silver, but also some cobalt? With cadmium the double compound, if formed, may be more readily broken up, hence the separation is easily made. By reducing the quantity of potassium cyanide with mercury and silver we afford no opportunity for the production of cobalticyanide in such quantity as to appreciably affect the deposition of the other metals.

Copper from Cadmium in the presence of Sulphuric Acid.

From the fact that it is possible to completely precipitate cadmium from the solution of its sulphate containing free sulphuric acid,[1] and as copper is also deposited under similar conditions, the separation of these metals when in this form would hardly be expected. The experiments given below show that notwithstand-

[1] Smith, this Journal **2**, 42.

ing all this, their separation can be effected under the conditions indicated. The first results were negative.

Experiment.—10 cc. copper sulphate (=0.1975 gram metallic copper), 10 cc. cadmium sulphate (=0.1828 gram cadmium), 1 cc. H_2SO_4 (sp. gr. 1.09), with 150 cc. water, were electrolysed with a current generating 0.4 cc. oxyhydrogen gas per minute. The copper was fully precipitated, and with it considerable cadmium.

In a second series of three experiments, similar to that above, excepting that the current only gave 0.22 cc. OH gas per minute, the copper was entirely precipitated, but carried down some cadmium with it.

In a third series of three experiments, the sulphuric acid in each dish was increased to 5 cc. (sp. gr. 1.09). The current gave 0.22 cc. OH gas per minute. The copper was not completely precipitated, and cadmium had deposited upon the copper.

The fourth series was made up as follows:

1st Exp. 10 cc. copper sulphate = 0.1975 gram copper, 10 cc. cadmium sulphate = 0.1828 gram cadmium, 10 cc. H_2SO_4 (sp. gr. 1.09), 100 cc. water. Current = 0.3 cc. OH gas per minute. Time 12 hours. The copper deposit weighed 0.1968 gram.

2d Exp. Same as 1. Copper found 0.1964 gram.

3d Exp. 10 cc. cadmium sulphate = 0.1828 gram cadmium. 5 cc. H_2SO_4 (sp. gr. 1.09). 100 cc. water. Current as in 1 and 2. Cadmium was not precipitated.

In the fifth series of four experiments, a current generating 0.5 cc. OH gas per minute was employed. The quantity of acid was increased to 10 cc. and 15 cc. Cadmium separated together with the copper.

The sixth series included five experiments:

Exp. 1. 10 cc. copper sulphate = 0.1975 gram copper, 10 cc. cadmium sulphate = 0.1828 gram cadmium, 15 cc. H_2SO_4 (sp. gr. 1.09), 100 cc. water. Current = 0.20 cc. OH gas per minute. Copper found was 0.1969 gram.

Exp. 2. Same as 1, gave 0.1976 gram copper.

Exp. 3. Same as 1 and 2, except that the current generated 0.3 cc. OH gas per minute. Copper found was 0.1975 gram.

Exps. 4 and 5 were like 3. The copper deposited equaled 0.1969 gram and 0.1962 gram.

Tabulating the results we have:

	Copper required.	Copper found.	Difference in percentage.
I.	0.1975 gram.	0.1968 gram.	—0.35 per cent.
II.	"	0.1964	—0.55
III.	"	0.1969	—0.30
IV.	"	0.1976	+0.05
V.	"	0.1975	...
VI.	"	0.1969	—0.30
VII.	"	0.1962	—0.65

The filtrates from the deposited copper were examined for that metal. VII showed a trace of copper. Cadmium was not detected in the precipitated metal. Holding strictly to the conditions given above will enable any one to effect the separation of these two metals in the presence of sulphuric acid.

UNIVERSITY OF PENNSYLVANIA, *January* 6, 1890.

Contributions from the Chemical Laboratory of Harvard College.

LXVIII.—ON CHLORPYROMUCIC ACIDS.

BY HENRY B. HILL AND LOUIS L. JACKSON.

[Continued from page 51.]

χ-DICHLORPYROMUCIC ACID.

The formation of the ethyl ether of this acid by the decomposition of ethyl pyromucic tetrachloride has already been described. The ether was recrystallised from hot alcohol, and saponified by alcoholic sodic hydrate. On the addition of hydrochloric acid to the aqueous solution of the sodium salt, a sparingly soluble acid separates, which may easily be purified by recrystallisation from hot water.

The acid dried over sulphuric acid gave, on analysis, the following results:

I. 0.2196 gram substance gave 0.2672 gram CO_2 and 0.0237 gram H_2O.

II. 0.2212 gram substance gave 0.3492 gram AgCl.

	Calculated for $C_5H_2Cl_2O_3$.	Found. I.	II.
C	33.15	33.18	...
H	1.10	1.20	...
Cl	39.22	...	39.03

χ-Dichlorpyromucic acid is readily soluble in ether or alcohol, and but sparingly soluble in cold water. In hot water it is freely soluble, and crystallises as the solution cools in long needles which melt at 197°–198°. The acid readily sublimes unchanged below its melting point. Sodium amalgam slowly reduces it to pyromucic acid melting at 129°–130°.

The solubility of the acid in water at 19.5° was determined in the usual manner. A solution of the acid saturated at 19.5° was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

I. 38.2670 grams solution saturated at 19.5° gave 0.0322 gram $BaSO_4$.

II. 37.5125 grams solution saturated at 19.5° gave 0.0301 gram $BaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of acid:

I.	II.
0 13	12

Baric χ-dichlorpyromucate, $Ba(C_5HCl_2O_3)_2.4H_2O$.—The barium salt may most readily be prepared by boiling the acid with baric carbonate. The salt is quite readily soluble in cold water, more soluble in hot water, and crystallises in columnar aggregations of prisms which contain four molecules of water. The crystallised salt is stable in the air, effloresces over sulphuric acid, and loses all its water at 100°.

I. 1.0471 gram air-dried salt lost at 100° 0.1285 gram H_2O.

II. 0.5464 gram air-dried salt gave 0.2235 gram $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2.4H_2O$.	Found. I.	Found. II.
H_2O	12.66	12.27	...
Ba	24.07	...	24.05

0.4495 gram salt dried at 100° gave 0.2091 gram $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2$.	Found.
Ba	27.56	27.35

The solubility of the salt in water at 19.5° was determined in the usual manner.

I. 11.1910 grams solution saturated at 19.5° gave 0.0820 gram $BaSO_4$.

II. 8.6544 grams solution saturated at 19.5° gave 0.0644 gram $BaSO_4$.

According to these determinations, the solution saturated at 20° contained the following percentages of anhydrous salt:

I.	II.
1.56	1.59

Calcic γ-dichlorpyromucate, $Ca(C_5HCl_2O_3)_2.4H_2O$.—The calcium salt was prepared by boiling the acid with calcic carbonate. The filtered solution was then concentrated on the water-bath to a small volume, and the salt which separated was filtered out and washed with a little water. Since the salt appeared to be about as soluble in cold water as in hot, it was dissolved in water and the solution concentrated *in vacuo* over sulphuric acid. The salt which separated was then pressed dry with filter paper. It is quite readily soluble in water, and crystallises in prisms which contain four molecules of water. The crystallised salt is permanent in the air, effloresces slowly over sulphuric acid, and loses all its water at 117°.

I. 0.9075 gram air-dried salt lost at 117° 0.1380 gram H_2O.

II. 0.6080 gram air-dried salt gave 0.1746 gram $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2.4H_2O$.	Found. I.	Found. II.
H_2O	15.25	15.21	...
Ca	8.48	...	8.44

0.3377 gram salt dried at 117° gave 0.1152 gram $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2$.	Found.
Ca	10.00	10.02

The solubility of the salt in water at 19.5° was determined in the usual manner. The calcium was precipitated as oxalate and ignited with sulphuric acid.

I. 6.5743 grams solution saturated at 19.5° gave 0.1522 gram $CaSO_4$.

II. 7.2115 grams solution saturated at 19.5° gave 0.1689 gram $CaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
6.81	6.89

Ethyl χ-dichlorpyromucate, $C_5HCl_2O_3C_2H_5$.—The process by which the ethyl ether was obtained has already been described. It is readily soluble in hot alcohol, sparingly soluble in cold alcohol, and crystallises in clustered prisms with rectangular truncations which melt at 72°–73°. A sample of the ether melting at 72°–73° was distilled under a pressure of 16 mm. and boiled constant at 122.5°, temperature of bath 170°–175°. For analysis the ether was dried over sulphuric acid.

I. 0.2034 gram substance gave 0.2790 gram AgCl.

II. 0.2302 gram substance gave 0.3160 gram AgCl.

	Calculated for $C_5HCl_2O_3C_2H_5$.	Found. I.	II.
Cl	33.98	33.91	33.94

In order to determine the constitution of this dichlorpyromucic acid we studied its oxidation products with aqueous bromine.

Action of Bromine and Water.

As it was desirable to compare the oxidation product obtained from this acid with that obtained from the βδ-dichlorpyromucic acid under the same conditions, the acid was suspended in five times its weight of water, somewhat more than four atoms of bromine added as rapidly as possible, and the solution boiled until the oil which was at first formed had nearly disappeared. The filtered solution was evaporated to dryness at a gentle heat, the crystalline residue dissolved in a little cold water, filtered, and again evaporated nearly to dryness. The acid which separated was readily soluble even in cold water, almost insoluble in hot chloroform or benzol. It was therefore pressed dry with filter paper and carefully extracted with hot benzol. The acid as thus prepared crystallised in microscopic crystals which melted at 188°–189°, and moreover gave on analysis the percentage of chlorine required by monochlorfumaric acid.[1]

0.1441 gram substance dried over H_2SO_4 gave 0.1377 gram AgCl.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.59	23.62

The χ-dichlorpyromucic acid, like the βδ-dichlorpyromucic acid,

[1] Kauder, loc. cit.

therefore gives with aqueous bromine as the chief product chlorfumaric acid according to the equation

$$C_5H_2Cl_2O_3 + 2Br_2 + 3H_2O = C_4H_2ClO_4 + CO_2 + HCl + 4HBr.$$

Since the oxidation with bromine had shown with sufficient precision that one of the chlorine atoms of the χ-dichlorpyromucic acid occupied the δ position, we thought it unnecessary for our purposes to study also the action of nitric acid.

Action of Fuming Sulphuric Acid.

The two isomeric dibrompyromucic acids had shown marked differences in their behavior toward fuming sulphuric acid.[1] While the $\beta\gamma$ acid had rapidly been converted into the corresponding sulphonic acid, brommaleic acid in nearly theoretical quantity had been formed from the $\beta\delta$-dibrompyromucic acid, and no trace of a sulphonic acid could be detected. Preliminary experiments proved that the $\beta\gamma$- and $\beta\delta$-dichlorpyromucic acids showed a similar difference in their behavior toward fuming sulphuric acid. While the formation of chlormaleic acid in the latter case could not definitely be proved, certainly no sulphonic had been formed, and it seemed to us of interest to study also the behavior of the third isomeric dichlorpyromucic acid under the same conditions. χ-Dichlorpyromucic acid dissolves readily in fuming sulphuric acid, and if care be taken to prevent any marked elevation of temperature no very essential decomposition ensues, although a slight effervescence is noticeable. After the solution of the acid in four times its weight of fuming sulphuric acid had stood for thirty-six hours, it was poured into a large amount of cold water, the solution cooled, and thoroughly extracted with ether. The ethereal extract left on evaporation a small quantity of a colorless oil which reduced silver oxide, and whose vapor vigorously attacked the eyes and nose. The amount of oil thus obtained was wholly insufficient for further study. On standing, it deposited a few clustered needles which probably were unaltered acid, although they may possibly have been the decomposition product subsequently described. From the aqueous solution the barium salt was prepared in the usual way, and, since the properties of the neutral salt were unfavorable to purification, it was converted into the acid salt, and this recrystallised from hot water. The acid salt was readily soluble in hot water,

[1] This Journal **10**, 386 and 421; and Proc. Am. Acad. **23**, 218.

more sparingly soluble in cold water, and crystallised in triclinic (?) prisms which effloresced on exposure to the air. It gave an excellent qualitative reaction for sulphur, and when dried over sulphuric acid[1] gave the percentage of barium required by the formula $Ba(C_5HCl_2SO_6)_2$.

0.3886 gram of the salt dried over sulphuric acid gave 0.1338 gram $BaSO_4$.

	Calculated for $Ba(C_5HCl_2SO_6)_2$.	Found.
Ba	20.84	20.24

Baric χ-dichlorsulphopyromucate, $BaC_5Cl_2SO_6.2H_2O$.—From the acid barium salt we prepared the neutral salt by neutralising its aqueous solution with baric carbonate. Since the hot saturated solution deposited little or nothing on cooling, it was evaporated *in vacuo* over sulphuric acid. The salt then crystallised in sheaves of prisms which appeared to be triclinic. It was permanent in the air, effloresced over sulphuric acid, and lost its water completely at 160°.

1.4159 gram of the air-dried salt lost at 160° 0.1277 gram H_2O.

	Calculated for $BaC_5Cl_2SO_6.2H_2O$.	Found.
H_2O	8.33	9.02

0.5296 gram of the salt dried at 160° gave 0.3126 gram $BaSO_4$.

	Calculated for $BaC_5Cl_2SO_6$.	Found.
Ba	34.59	34.69

The formation of a dichlorsulphopyromucic acid by the action of fuming sulphuric acid upon the χ-dichlorpyromucic acid is thus sufficiently established. The bromsulphopyromucic acids are so readily reduced in alkaline solution that we hoped to be able to prepare from this dichlorsulphopyromucic acid the corresponding sulphopyromucic acid, and thus establish the position of the two chlorine atoms. We soon found, however, that the chlorine was held with unusual persistence, and with the material at our disposal we have as yet been unable to reach decisive results.

[1] The single determination of the water of crystallisation was unfortunately defective. It gave 13.34 per cent. of water in the salt dried by short exposure to the air, while a salt crystallising with 2½ molecules of water should contain 13.70 per cent.

Decomposition by Hydrochloric Acid.

If the γ-dichlorpyromucic acid is heated with water in a sealed tube to 170°, no change is effected, but a reaction which we had in no way anticipated takes place if it is heated upon the water-bath in an open flask with concentrated hydrochloric acid. Carbonic acid is evolved, and in a short time the acid is completely decomposed with the formation of a neutral body which volatilises when the solution is boiled, and which can be extracted, although with difficulty, from the distillate, or from the original solution with ether. The ethereal solution left on evaporation a white crystalline solid which was sparingly soluble in water, readily soluble in cold chloroform or benzol, and but sparingly soluble in ligroin. When recrystallised from ligroin it formed long slender lustrous prisms, which melted at 52°–53°, and sublimed rapidly at ordinary temperatures. It reduced argentic oxide on warming, and dissolved in aqueous alkalies, forming a yellow solution. The physical properties and the behavior of this substance at once recalled to our minds the crystalline body melting at 77° which Hill and Sanger[1] had obtained in small quantity from the by-products of the decomposition of pyromucic tetrabromide by alcoholic sodic hydrate. The formula of this body had been shown to be $C_4H_3BrO_2$, and an analysis of the new substance left no doubt of its similar composition.

0.1045 gram substance gave 0.1261 gram AgCl.

	Calculated for $C_4H_3ClO_2$.	Found.
Cl	29.95	29.84

This interesting body is probably formed according to the reaction

$$C_5H_3Cl_3O_3 + H_2O = C_4H_3ClO_2 + CO_2 + HCl.$$

And since we found little difficulty in obtaining 40 per cent. of the yield which this equation demands, it will be possible to study it more in detail. Unfortunately, it was discovered so late in our work as to make it impossible to present the results of such a study in this paper. While it would be easy for us to venture a conjecture as to its structure, we prefer to await the results of a future investigation.

[1] Proc. Am. Acad. 21, 158.

Trichlorpyromucic Acid.

For the preparation of the trichlorpyromucic acid it was evidently most convenient to decompose with alkalies the tetrachloride of the δ-chlorpyromucic acid. It did not seem necessary, however, to prepare this tetrachloride in a pure condition, and indeed we first obtained the trichlorpyromucic acid from one of the earlier preparations of the ethyl pyromucic tetrachloride in which an unusually great spontaneous elevation of temperature had taken place through the rapid absorption of chlorine. For its preparation we heated the ethyl pyromucate to 145°, and passed in chlorine at this temperature until the gain in weight showed that one atom of hydrogen had been replaced by chlorine. We then allowed the temperature to fall to about 120°, and continued the chlorination to saturation. The total gain in weight then corresponded approximately to that required by the formation of the tetrachloride of the ethyl chlorpyromucate. On decomposing this product as usual with a cold concentrated alcoholic solution of sodic hydrate, the alcoholic solution filtered from the insoluble sodium salts contained, as in the previous cases, small quantities of liquid furfuran derivatives, but the amount was so minute that no separate study of them was made. The sodium salts dissolved in hot water gave with hydrochloric acid an impure trichlorpyromucic acid as a more or less colored oil, which solidified as the solution cooled. For the purification of the acid we have found it convenient to take advantage of the slight solubility of the ammonium salt in cold water. The crude acid was suspended in about thirty times its weight of water, ammonic hydrate added in excess, and the hot solution treated with bone-black. The filtered solution deposits on cooling the greater part of the trichlorpyromucic acid as the ammonium salt from which the pure acid can readily be obtained. The small amount of trichlorpyromucic acid remaining in the ammoniacal solution may be recovered, although at the expense of considerable trouble, by precipitation with calcic chloride and repeated recrystallisation from water and dilute alcohol of the acid obtained from the insoluble calcium salt.

The yield of pure trichlorpyromucic acid was far from satisfactory, as we could obtain only 30 per cent. of the weight of the ethyl pyromucate taken, but 15 per cent. of the theoretical amount.

For analysis the acid was dried over sulphuric acid.

I. 0.3214 gram substance gave 0.3248 gram CO_2 and 0.0211 gram H_2O.

II. 0.2107 gram substance gave 0.4192 gram AgCl.

III. 0.2135 gram substance gave 0.4255 gram AgCl.

	Calculated for $C_5HCl_3O_3$.	Found. I.	II.	III.
C	27.85	27.56	...	...
H	0.46	0.73	...	...
Cl	49.43	...	49.19	49.27

Trichlorpyromucic acid is readily soluble in alcohol or ether, quite readily soluble in boiling benzol, and but sparingly soluble in cold benzol. Hot water dissolves it but sparingly, and as the solution cools, most of the acid is deposited in microscopic needles which melt at 172°–173°. This melting point was so much below that which we had been led to expect from analogy to the known acid containing bromine that we felt some doubt of its correctness, more especially since the crude acid was so far from pure. A sample of the acid melting at 172°–173° was therefore recrystallised twice from water and then three times from benzol, without perceptibly changing the melting point. The acid was then converted into the calcium salt, and this separated by crystallisation into three successive fractions. The acid from these three fractions melted simultaneously and sharply at 172°–173°. Finally, the ethyl ether was made, and the acid prepared from the repeatedly recrystallised pure ether melted at the same point.

The solubility of the acid in water at 19.5° was determined by boiling with baric carbonate a weighed quantity of a solution of the acid saturated at that temperature, and determining the barium dissolved as sulphate.

I. 49.1742 grams solution saturated at 19.5° gave 0.0344 gram $BaSO_4$.

II. 47.0228 grams solution saturated at 19.5° gave 0.0331 gram $BaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of acid:

I.	II.
0.13	0.13

Baric trichlorpyromucate, $Ba(C_5Cl_3O_3)_2.4H_2O$.—The barium salt was prepared by precipitating a dilute solution of the am-

monium salt with baric chloride, and recrystallising the sparingly soluble salt thus thrown down from hot water. The salt proved to be but sparingly soluble even in hot water, and still less soluble in cold water. It separates from a hot concentrated solution in needles which apparently contain four molecules of water. The salt is permanent in the air, but loses three molecules of its crystal water over sulphuric acid. When dried at 120° it still retains a half-molecule of water, which cannot be expelled without essential decomposition.

I. 0.6847 gram air-dried salt gave 0.2511 gram $BaSO_4$.

II. 0.6205 gram air-dried salt gave 0.2273 gram $BaSO_4$.

III. 0.5672 gram air-dried salt gave 0.2076 gram $BaSO_4$.

IV. 1.3625 gram air-dried salt lost over H_2SO_4 0.1148 gram H_2O, and at 120° 0.1338 gram H_2O.

V. 1.1645 gram air-dried salt lost over H_2SO_4 0.1003 gram H_2O, and at 100° 0.1124 gram H_2O.

VI. 1.3000 gram air-dried salt lost over H_2SO_4 0.1124 gram H_2O and at 100° 0.1256 gram H_2O.

	Calculated for $Ba(C_5Cl_3O_3)_2.4H_2O$.	Found. I.	II.	III.	IV.	V.	VI.
Ba	21.47	21.56	21.54	21.52	...	...	...
$3H_2O$	8.46	...	...	...	8.43	8.61	8.65
$3\frac{1}{2}H_2O$	9.87	...	...	...	9.83	9.65	9.66

I. 0.7484 gram substance dried at 120° gave 0.3038 gram $BaSO_4$.

II. 0.6247 gram substance dried at 100° gave 0.2521 gram $BaSO_4$.

III. 0.6497 gram substance dried at 100° gave 0.2634 gram $BaSO_4$.

	Calculated for $Ba(C_5Cl_3O_3)_2.\frac{1}{2}H_2O$.	Found. I.	II.	III.
Ba	23.83	23.86	23.72	23.84

The solubility of the salt in water at 19.5° was determined in the usual way.

I. 41.4499 grams solution saturated at 19.5° gave 0.0470 gram $BaSO_4$.

II. 44.9822 grams solution saturated at 19.5° gave 0.0500 gram $BaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
0.27	0.27

Calcic trichlorpyromucate, $Ca(C_5Cl_3O_3)_2.4H_2O$.—The calcium salt was prepared by precipitating a dilute solution of the ammonium salt with calcic chloride. The precipitated salt was then crystallised from hot water, and proved to be sparingly soluble in hot water, still less soluble in cold water, and separated from a hot solution in irregular aggregations of small leafy plates.

The salt is permanent in the air, effloresces over sulphuric acid, and loses all its water at 110°.

I. 1.3008 gram air-dried salt lost at 110° 0.1697 gram H_2O.

II. 1.8389 gram air-dried salt lost at 110° 0.2417 gram H_2O.

	Calculated for $(C_5Cl_3O_3)_2Ca.4H_2O$.	Found. I.	II.
H_2O	13.30	13.05	13.14

I. 0.6399 gram salt dried at 110° gave 0.1855 gram $CaSO_4$.

II. 0.6974 gram salt dried at 110° gave 0.2019 gram $CaSO_4$.

	Calculated for $Ca(C_5Cl_3O_3)_2$.	Found. I.	II.
Ca	8.53	8.53	8.51

The solubility of the salt in water at 19.5° was determined in the usual manner. The calcium was precipitated as oxalate, and the oxalate ignited with sulphuric acid.

I. 18.1457 grams solution saturated at 19.5° gave 0.0342 gram $CaSO_4$.

II. 14.6806 grams solution saturated at 19.5° gave 0.0265 gram $CaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
0.65	0.62

Potassic trichlorpyromucate, $KC_5Cl_3O_3$.—The potassium salt was prepared by boiling the acid with a slight excess of potassic carbonate. The solution was then concentrated until the salt began to separate, and on cooling it solidified to a mass of crystals, which were filtered off on the pump and pressed dry with filter paper. The salt is readily soluble even in cold water, and separates from a hot concentrated solution in sheaves of fine needles, which lose nothing in weight when heated to 120°. Analyses of the salt dried at this temperature proved it to be anhydrous.

I. 0.5338 gram salt dried at 120° gave 0.1851 gram K_2SO_4.

II. 0.4425 gram salt dried at 120° gave 0.1532 gram K_2SO_4.

	Calculated for $KC_5Cl_3O_3$.	Found. I.	II.
K	15.42	15.57	15.54

Argentic trichlorpyromucate, $AgC_5Cl_3O_3$.—The silver salt may best be prepared by precipitating a hot solution of the calcium salt with argentic nitrate. For analysis the precipitated salt was well washed, and then recrystallised from hot water. It is sparingly soluble even in hot water, less soluble in cold water, and crystallises from a hot concentrated solution in moss-like aggregations of fine needles.

The air-dried salt gave on analysis much too low a percentage of silver, and although the sample analysed was free from calcium salt and free acid, it failed to give perfectly satisfactory results even when dried *in vacuo* over sulphuric acid or at 100°.

I. 0.5142 gram salt dried *in vacuo* over H_2SO_4 gave 0.2254 gram AgCl.

II. 0.4545 gram salt dried at 100° gave 0.1998 gram AgCl.

	Calculated for $C_5Cl_3O_3Ag$.	Found. I.	II.
Ag	33.48	33.00	33.10

Ethyl trichlorpyromucate, $C_5Cl_3O_3C_2H_5$.—The ethyl ether was prepared in the usual manner, by warming an alcoholic solution of the acid with concentrated sulphuric acid. 5 parts of the acid, 10 parts of absolute alcohol, and 5 parts of concentrated sulphuric acid (sp. gr. 1.84) were heated together for three hours at 100°. The ether was then precipitated with water, washed with warm dilute sodic carbonate, and finally with water. The ether is readily soluble in hot alcohol, more sparingly in cold alcohol, and crystallises is flat prisms which melt at 62°–63°.

I. 0.2142 gram substance dried over H_2SO_4 gave 0.3793 gram AgCl.

II. 0.2536 gram substance dried over H_2SO_4 gave 0.4476 gram AgCl.

	Calculated for $C_8Cl_3O_3C_2H_5$.	Found. I.	II.
Cl	43.74	43.77	43.64

Trichlorpyromucamide, $C_5Cl_3O_2NH_2$.—Concentrated aqueous ammonia attacks the trichlorpyromucic ether but slightly at ordinary temperatures. Even after three hours' heating in a sealed tube at 100° most of the ether was found to be unaltered, and we were obliged to prepare the amide from the acid chloride by the action of solid ammonic carbonate. The amide is but spar-

ingly soluble even in hot water, and crystallises in long slender needles which melt at 160°–161°.

0.3804 gram substance dried over H_2SO_4 gave 23.2 cc. moist N at 21° under a pressure of 765 mm.

	Calculated for $C_5Cl_3O_3NH_3$.	Found.
N	6.53	6.95

Although there could be no doubt as to the constitution of the trichlorpyromucic acid, it seemed better for the sake of completeness to study its behavior with oxidising agents.

Action of Bromine and Water.

Trichlorpyromucic acid was suspended in ten times its weight of cold water, and a little more than one molecule of bromine was added. Carbonic dioxide was evolved and the color of the bromine rapidly disappeared. When the reaction had been completed, a white insoluble substance remained, which was removed by filtration and washed with a dilute solution of sodic carbonate. The alkaline solution gave on acidification a copious precipitate of unaltered trichlorpyromucic acid, whose identity was established by the melting point 172°–173°. The substance which remained undissolved by the alkaline solution had the characteristic odor of the tetrabromfurfuran, and crystallised from hot alcohol in irregular plates which melted at 75°–76°. Analysis showed this substance to be a trichlorbromfurfuran.

I. 0.1749 gram substance dried over H_2SO_4 gave 0.4269 gram AgCl and AgBr.

II. 0.1411 gram substance dried over H_2SO_4 gave 0.3447 gram AgCl and AgBr.

	Calculated for C_4Cl_3BrO.	Found. I.	Found. II.
$Cl_3 + Br$	74.45	73.60	73.67

The strongly acid filtrate from the trichlorbromfurfuran and unaltered trichlorpyromucic acid yielded on extraction with ether a crystalline acid which was readily soluble in water. The amount of this acid was too small for analysis, but it was easily identified as dichlormaleic acid by the melting point of its anhydride, 119°–120°.[1]

The reaction had therefore taken place in accordance with the following equations:

[1] Ciamician and Silber, *loc. cit.*

$$C_5HCl_3O_3 + Br_2 = C_4Cl_3BrO + CO_2 + HBr.$$
$$C_5HCl_3O_3 + 2Br_2 + 3H_2O = C_4H_3Cl_2O_4 + CO_2 + HCl + 4\,HBr.$$

Action of Nitric Acid.

Trichlorpyromucic acid is but slowly attacked by nitric acid, and prolonged heating with moderately strong nitric acid is needed for complete oxidation. Even after heating the acid for six hours with six times its weight of nitric acid (sp. gr. 1,42) diluted with an equal weight of water, a portion of the trichlorpyromucic acid escaped oxidation. Carbonic dioxide was slowly given off, and a small quantity of an insoluble oil was formed, which had a peculiar penetrating odor not unlike that of substituted furfuran derivatives. Its quantity was too small to admit of its identification. In solution we were able to find nothing but dichlormaleic acid, which we purified through the barium salt and identified by the melting point of its anhydride and by analysis.

0.1997 gram substance dried over H_2SO_4 gave 0.3086 gram AgCl.

	Calculated for $C_4H_3Cl_2O_4$.	Found.
Cl	38.38	38.20

The reaction had therefore taken place in accordance with the following equation:

$$C_5HCl_3O_3 + 2O + H_2O = C_4H_3Cl_2O_4 + CO_2 + HCl.$$

We have also prepared several other trisubstituted pyromucic acids, which may conveniently be described here.

$\beta\gamma$-Dichlor-δ-Brompyromucic Acid.

Hill and Sanger[1] found that $\beta\gamma$-dibrompyromucic acid was easily converted into tribrompyromucic acid by the action of bromine at ordinary temperatures.

If $\beta\gamma$-dichlorpyromucic acid is exposed to the vapors of bromine at ordinary temperatures, bromine is rapidly absorbed, hydrobromic acid is evolved, and the gain in weight approaches that required by the displacement of hydrogen by bromine. The product was treated with small quantities of boiling water to remove unaltered dichlorpyromucic acid, and then recrystallised from

[1] Proc. Am. Acad. **21**, 172.

dilute alcohol and finally from water. The acid is readily soluble in alcohol or ether, dissolves freely in boiling benzol, more sparingly in cold benzol. Even in boiling water it is very sparingly soluble. It crystallises in short clustered prisms which melt at 185°–186°.

0.3189 gram substance dried over H_2SO_4 gave 0.5817 gram AgCl and AgBr.

	Calculated for $C_5HCl_2BrO_3$.	Found.
$Cl_2 + Br$	58.08	57.99

βγ-Dibrom-δ-Chlorpyromucic Acid.

This acid we made by treating the ethyl βγ-dibrompyromucate with chlorine and decomposing the product with alcoholic sodic hydrate. On acidifying the aqueous solution of the sodium salts thus obtained, a crystalline acid was precipitated, which after one recrystallisation from dilute alcohol melted at 192°–193°. After recrystallisation from benzol the melting point rose to 193°–194°. The acid was readily soluble in alcohol, ether, or hot benzol, sparingly soluble in cold benzol, or even in boiling water.

0.2315 gram substance dried over H_2SO_4 gave 0.3960 gram AgCl and AgBr.

	Calculated for $C_5HClBr_2O_3$.	Found.
$Cl + Br_2$	64.19	64.37

We have attempted to prepare these acids also by the decomposition with alcoholic sodic hydrate of products formed by the addition of bromine to δ-chlorpyromucic acid and of chlorine to ethyl δ-brompyromucate. Although we readily prepared in this way trisubstituted acids, the products in neither case were homogeneous, tribrom- or trichlorpyromucic acids being formed together with the acid containing both halogens.

βγ-Dichlor-δ-Nitropyromucic Acid.

Hill and Palmer[1] have shown that βγ-dibrompyromucic acid is easily converted into a sulphonic acid by means of sulphuric acid, and that the sulpho group in this acid may readily be replaced by the nitro group. βγ-dichlorpyromucic acid was dissolved in fuming sulphuric acid, and the barium salt of the sulphonic acid isolated in the usual way. Since a more complete study of the

[1] This Journal **10**, 386, 390; and Proc. Am. Acad. **23**, 201, 205.

salt did not fall within the plan of our work, we precipitated the barium exactly with sulphuric acid, and evaporated the dilute solution of the acid first at 100° and afterwards *in vacuo* over sulphuric acid. The crystalline, somewhat deliquescent acid thus obtained was dissolved in several times its weight of fuming nitric acid, to which half its volume of concentrated sulphuric acid had been added. After the action was finished, the nitric acid was partially expelled, the residue diluted with water and extracted with ether. The ether was then shaken with a dilute solution of sodic carbonate, and the acid precipitated from this alkaline solution by the addition of hydrochloric acid. The ethereal solution proved to contain no substance which invited farther investigation.

The $\beta\gamma$-dichlor-δ-nitropyromucic acid is readily soluble in alcohol, ether, or hot benzol. Hot water dissolves it freely, and on cooling, the greater part of the acid is deposited in flattened leafy prisms which melt at 189°–190°.

0.2168 gram substance dried over H_2SO_4 gave 0.2756 gram AgCl.

	Calculated for $C_5HCl_2NO_5$.	Found.
Cl	31.42	31.42

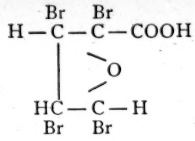
We have as yet made no further study of this acid.

Theoretical Considerations.

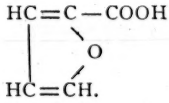
The acids melting at 168°–169° and 155°–156°, which in the preceding pages we have called the $\beta\gamma$ and $\beta\delta$ dichlorpyromucic acids, are without doubt identical in structure with the two dibrompyromucic acids described by Hill and Sanger.[1] Their physical properties and the solubility of their salts show their close relationship to these bromine derivatives, while the products formed from them by oxidation conclusively prove that they are structurally isomeric, and that the chlorine atoms occupy the same relative position that the bromine atoms hold in the dibrompyromucic acids. On reduction these two acids both yield the same chlorpyromucic acid, which in its turn closely resembles the β-brompyromucic acid in its physical properties, although its melting point, 145°–146°, is comparatively high. It is to be noted, however, that the $\beta\gamma$-dichlorpyromucic acid alone is formed by the action of alkalies

[1] Proc. Am. Acad. **21**, 137.

upon the ethyl pyromucic tetrachloride, while the two isomeric dibrompyromucic acids are simultaneously formed under similar conditions. This simultaneous formation of the two structurally isomeric acids from pyromucic tetrabromide to which the formula



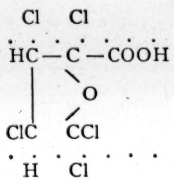
may be assigned, led Hill and Sanger[1] to the conclusion that these acids must have their bromine atoms in the $\beta\gamma$ and $\beta\delta$ positions respectively, and that pyromucic acid itself probably had the formula



The structure of the $\beta\gamma$ and $\beta\delta$ dichlorpyromucic acids seems to us to be thus sufficiently established.

As to the third isomeric form, which for the present we have called the χ-dichlorpyromucic acid, since it gives chlorfumaric acid by oxidation, it is evident that it must either have its chlorine atoms in the γ and δ positions, or that it must be a geometrically isomeric form of the $\beta\delta$ acid. Unfortunately, we have been able to obtain as yet no evidence which conclusively proves either view to be correct. A dichlorpyromucic acid having its chlorine atoms in the γ and δ positions could not well be formed from ethyl pyromucic tetrachloride by the simple loss of hydrochloric acid. Tönnies[2] had shown that δ-brompyromucic acid could be formed by the action of heat upon pyromucic tetrabromide, when bromine must be eliminated as well as hydrobromic acid. Since we had noticed that hydrochloric acid invariably was evolved in the preparation of ethyl pyromucic tetrachloride, it seemed to us not improbable that the χ-dichlorpyromucic acid was in fact the $\gamma\delta$ acid which had been formed in a similar way from the tetrachloride of the δ-chlorpyromucic ether necessarily contained in the crude product.

[1] Ber. d. chem. Ges. **11**, 1088. [2] Proc. Am. Acad. **11**, 182.



We found, however, that no χ-dichlorpyromucic acid was formed on heating ethyl δ-chlorpyromucic tetrachloride, and that our product in this case contained the $\beta\delta$ acid alone, so that the molecule of chlorine, which had been eliminated in the reaction, had taken its chlorine atoms from the γ and δ positions. We hoped also to get further evidence as to the structure of the χ-dichlorpyromucic acid by reducing it to a chlorpyromucic acid, or by substituting the chlorine of the χ-dichlorsulphopyromucic acid by hydrogen; but in neither case have we yet succeeded in obtaining well characterised products.

While it seems to us probable that the χ-dichlorpyromucic acid is geometrically isomeric with the $\beta\delta$ acid, we have as yet been unable to convert one acid into the other. Both acids volatilise unchanged when heated, and the ordinary reagents which usually effect conversion in such cases have failed to bring about any perceptible isomerisation. While lack of material has to a great degree limited our work with the χ acid, we have studied the behavior of the $\beta\delta$ acid under a variety of conditions, with purely negative results. If the two acids are in fact geometrically isomeric, the simultaneous appearance of both forms in the distillation of ethyl pyromucic tetrachloride with the escape of large quantities of hydrochloric acid shows that the conversion of one acid into the other is effected with difficulty, while the formation of the $\beta\delta$ acid alone from the ethyl δ-chlorpyromucic tetrachloride under similar conditions is especially worthy of note. Since pyromucic acid apparently contained two pairs of carbon atoms doubly tied, the existence of geometrically isomeric forms of its derivatives seemed at the outset more than probable, and during the progress of the investigations which for many years have been carried on in this laboratory, careful search had been made for such bodies, but hitherto only the two isomeric dibromfurfuran tetrabromides of Hill and Hartshorn[1] had been discovered. Since the discovery of

[1] Ber. d. chem. Ges, **18**, 450.

the χ-dichlorpyromucic acid, which we made toward the close of our work, we have attempted to prepare the corresponding bromine derivative, but as yet without success. The isolation of the body $C_4H_3BrO_2$, which Hill and Sanger[1] found among the products of the decomposition of pyromucic tetrabromide by alkalies, certainly is an indication of the previous existence of such an acid, although it is by no means clear in what stage of the process the decomposition of the acid was effected, nor how the decomposition product itself escaped further alteration. Any detailed consideration of the geometrical structure of pyromucic acid we feel obliged to postpone until more facts bearing upon the question are at our disposal.

REVIEWS AND REPORTS.

Osmotic Pressure and the Determination of Molecular Weights.

Within recent years it has become more and more apparent that an intimate connection exists between the stoechiometrical composition of a solution and its physical behavior. While earlier efforts towards proving this assumption were unsuccessful, chiefly because the experimental material was almost wholly confined to aqueous solutions of salts, which offer peculiar obstacles to such an investigation, F. Raoult's[2] patient researches upon organic substances in more varied solutions have enabled him to formulate accurately the long-expected laws, and to put the chemical world under lasting obligation for new methods for determining molecular weights under very favorable conditions. Raoult's law would read, in its most general form: In dilute solutions the depressions of the vapor tension and of the freezing point of the solvent vary directly with the ratio between the numbers of molecules of solvent and of substance dissolved in the mixture. Provided there be no chemical action involved in the process of solution, this relation is entirely independent of the nature of the substances.

Within the ordinary range of conditions, the *freezing point* of a pure liquid is constant; according to Raoult's law, every molecule of foreign matter occasions the same constant depression. Every liquid, however, has its own constant coefficient of depres-

[1] Proc. Am. Acad. **21**, 158. [2] C. R. **87**, 167; **44**, 1431.

sion, which may be found by determining the depression caused by the presence of one molecule of any substance in 100 molecules of the liquid.

The *vapor tension* of a liquid is not constant within the range of ordinary experimentation, since it is a complex function of the temperature and of the nature of the substance. But Raoult has shown that its depression shows a relation to percentage of foreign molecules which is independent of temperature, provided he expresses the depression, not in absolute measure, but as a fraction of the tension of the pure solvent at the same temperature. Then the molecular depression, *i. e.* the product of the molecular weight of the substance dissolved into the relative depression of a 1 per cent. solution, becomes a definite constant for any substances which that particular liquid may dissolve. It is noticeable that this constant's numerical value always approaches very nearly $\frac{1}{100}$ of the molecular weight of the solvent. The constant is therefore likewise independent of the nature of the solvent; one may generalise for *all* solutions, that the tension of the pure solvent is to the actual depression as is the number of molecules of solvent to the number of molecules of substance dissolved.

Laws as simple as these point to conditions, in solutions, very like those existing in the gaseous state. How great this analogy is, has been shown in the well matured papers of J. H. van't Hoff[1] on osmotic pressure. Osmotic pressure is the name given by van't Hoff to the force with which a liquid will enter into a cell containing the solution of some substance in that liquid through walls which are pervious to the solvent alone. Pfeffer[2] had shown that when such a cell is put into a vessel containing the pure solvent, the latter will enter the cell, increasing the bulk of the solution within, until this tendency is counterbalanced by the difference of level in the two vessels or some other pressure. The pressure required to counterbalance this tendency toward endosmose is always the same for the same concentration of the solution, and for different concentrations is found to be proportionate to the number of molecules dissolved in the unit volume. Whether this osmotic pressure be due to the motions of the dissolved molecules or to the attraction of some other sort which they exert upon the solvent, it is evident that the effect must depend upon the number of molecules per unit volume only when the molecules of the dissolved body are free to act independently of each other, as do the molecules of a gas. What the real kinetic energy of the molecules in such a solution is, we do not decide by drawing this conclusion. Even if it be as great as in a gas, the great resistance which a solvent opposes to diffusion shows that there is a force which greatly diminishes the external effect of this kinetic energy; it can never, therefore, have occurred to van't Hoff to claim that osmotic pres-

[1] Zeit. phys. Chem. **1**, 481.
[2] Monograph: Osmotische Untersuchungen. Leipzig, 1877.

sure is to be measured externally in the same absolute unit as gaseous pressure. But this opinion seems to have gained a foothold, so that the kinetic treatment of the subject is combated by M. Pupin,[1] on the ground that the kinetic energy of the molecules in a solution ought to burst the containing vessel when it was concentrated to what would correspond, in the gaseous state, to a volume under the pressure of many atmospheres. For this reason he demands that osmotic pressure should be treated as a *static* phenomenon. To the writer, Dr. Pupin appears to confound *molar* and *molecular* kinetics. Because the mass as a whole is in equilibrium and at rest, it does not follow that the molecules must be; in fact, very few physicists would care to call any force *static* in the sense that it was not occasioned by kinetic forces held in equilibrium for the moment.

That the vessel is not exploded by the pressure of the molecules, as Dr. Pupin demands, is due to the same force of solution which prevents their evaporating at the free surface. How great this force can become we may guess from the enormous condensation taking place in the absorption of gases by liquids; that the force is a *kinetic* one is shown by its being a function of temperature, a purely kinetic phenomenon. Bredig[2] has recently endeavored to show how this force can be made to diminish the external effect of the kinetic energy of the molecules of dissolved substance in such a manner that there is still freedom of action within the mass; and upon this line of reasoning we must depend for a final explanation of the phenomena.

For van't Hoff it was, however, sufficient that an osmotic pressure does exist which is dependent upon the kinetic energy of the molecules. By simple application of the method of Carnot's cycle, he shows that the osmotic pressure must be proportional to the absolute temperature, and that, for solutions of gases, it corresponds precisely to the tension of the gas in the solution. A natural inference from all this is that Boyle's, Gay-Lussac's, Henry's and Avogadro's laws find their counterparts in the laws governing osmotic pressure.

Suppose now solutions of two different substances in the same solvent to possess the same tension for the vapor of the latter; it is necessary that they shall also have the same osmotic pressure. For suppose them separated by a wall which is permeable to the solvent alone, but with their free surfaces in communication through the atmosphere. The vapor tension of both being the same, a little of the solvent might distill from one solution to the other without the performance of any work; but if at the same time their osmotic pressure were different, work *would* be performed by the retransfer of the same quantity of solvent through the membranous wall; this would mean a continuous process in an isolated system,

[1] Dissertation: Der osmotische Druck, etc. Berlin, 1889.
[2] Zeitschr. für phys. Chem. **4**, 444.

attended by gain or loss of energy. As this is impossible, equal vapor tension means equal osmotic pressure, and vice versa. Consequently the same number of molecules always produce the same depression of vapor-tension in a solvent. Exactly the same sort of reasoning would show that solutions having the same freezing point have like osmotic pressures. Both of these laws are identical with those found empirically by Raoult. Thermodynamic reasoning further shows that the molecular depression of vapor tension is indeed one hundredth of the molecular weight of the solvent, while the depression of the freezing point depends more directly upon the nature of the solvent, being a function of its latent heat of liquefaction: $t = 0.02 \frac{T^2}{W}$, where T is the absolute temperature of congelation of the pure solvent, W is the latent heat per kilogram, and t is the molecular depression.

These are the main results of van't Hoff's deductions, as far as molecular weight determinations are concerned. They enable us to employ for this purpose, with perfect confidence, observations upon the phenomena of evaporation, freezing, and osmose.

The direct measurement of osmotic pressure, as was done by Pfeffer, is difficult and not universally feasible. On the other hand, de Vries has shown how to compare such pressures by means of plant cells.[1] It is found that the living protoplasm of such cells, placed in a solution whose solvent only can penetrate the membrane, will yield water to the solution if the latter be concentrated, while it will take it up again if the solution is diluted. The protoplasm will therefore recede from the walls of its cell, or again approach it, and this expansion and contraction can be observed with the microscope. By systematic dilution, a point may be determined for every substance where it is isotonic with another, *i. e.* will neither expand nor contract a protoplasm which had come to rest in the other. Interesting as this method is, and capable of yielding good results in the hands of a skillful microscopist, it is hardly useful in the chemical laboratory where, aside from lack of familiarity with microscopic work, the investigator would be hampered by the exclusion of all substances which will kill plant life.

The freezing-point method has recently been reviewed in this magazine; it therefore only remains for the writer to express his view of its scope. While originally only those few liquids were used as solvents whose freezing points approached that of water, recent investigators have successfully employed substances like paraffine and the more fusible metals as the solvent; there are, therefore, few substances which are not amenable to the

[1] Pringsheim's Jahrbücher für Wissenschaftl. Botanik **14**, 4. See also Zeitsch. f. phys. Chemie **2**. 414. Donders and Hamburger have shown that the same phenomena can be studied in the behavior of blood-corpuscles; Archiv für Anatomie und Physiologie, Physiolog. Abth. 1886, p. 476, also Hamburger, Maandblad voor Natuurwetenschapen, 1889, p. 63.

method. But the following errors should be avoided: the use of thermometers not sufficiently sensitive to admit of observations at high dilutions; contenting oneself with observations within too limited a range of concentration to exclude a chance of overlooking abnormal behavior at some point; allowing too great a change of concentration to occur through the separation of the solvent in the solid state; using solvents which have a chemical effect upon the substance under investigation. Substances dissociate in one liquid which remain in complexer molecules in another. Chemists, in applying Raoult's methods, must remember that all electrolytes behave abnormally in aqueous solutions, and that the presence of hydrates may affect the result.

The method of determining the molecular weight from the vapor tension of the solution is not yet applied so generally; but its scope is even greater, because the range of solvents and of temperatures is so largely increased. Raoult and Planck[1] have shown independently of each other that the formula for the molecular weight of the dissolved substance is

$$M = M_0 \frac{p f'}{f - f'},$$

where M_0 is the molecular weight of the solvent, p the percentage of substance in 100 grams of solvent, f and f' the tensions of the pure solvent and the solution respectively.

Raoult measures f and f' by the heights of the mercury in eudiometers containing the liquids. A knowledge of the true value of p depends upon the determination of f', as part of the solvent leaves the solution as vapor under that tension; therefore an error in determining f' affects the result three times in the same direction. The method is less exact and more inconvenient than that of determining the freezing point.

A dynamic way, applied under Ostwald's direction by Walker,[2] is very much easier: determine the amount of water which different solutions will yield to the same amount of air. The measurements are made on the balance, and the apparatus consists of one set of bulbs to contain the solution, another to hold an absorbent for water, and an aspirator. The method has been generalised by Will and Bredig[3] for other solvents.

Lowering the tension means raising the point of ebullition for normal pressure, and the boiling point is, of course, capable of most exact determination. The method has been elaborated by Beckmann,[4] while the reader will remember a recent paper by Wiley on this subject, which does not, however, give sufficient details, as Beckmann's paper had already been announced.

The latter's apparatus consists of a vessel of about 100 cc. capacity, having a rounded bottom and three necks. Of these,

[1] Zeitschrift phys. Chem. **2**, 353 seq., 405 seq.
[2] Zeitschrift phys. Chem. **2**, 602.
[3] Berichte **20**, 1084.
[4] Zeitschrift phys. Chem. **4**, 532.

the central one connects with a Soxhlet condenser, the second carries a Beckmann thermometer, whose bulb is completely submerged, and the third neck serves for the introduction of the substance.

Steady boiling is assured by filling the vessel to a certain height with beads or garnets, and by sealing platinum wires into the bottom to promote conduction. The pure solvent is first raised to the boiling point, its temperature noted, and the weighed substance is thereupon introduced. As soon as the thermometer has become constant, the rise is noted; a fresh quantity of substance may then be introduced, and the observation repeated. The formula for the molecular elevation of the boiling point is precisely like that found by van't Hoff for the freezing point,

$$t = \frac{0.02\,T^2}{W},$$

with the exception that here T means the boiling point of the pure liquid and W its heat of vaporisation. The constant t being found by calculation or experiment, whenever we determine that for p grams of substance to 100 grams of solvent there is an elevation e, the molecular weight of the substance being M,

$$M = \frac{pt}{e}.$$

The experimental data to show the value of this method have not been published as yet, but it appears to be destined to play as great a part as does the freezing-point method introduced in its most convenient form by the same chemist.

MORRIS LOEB.

LES ORIGINES DE L'ALCHIMIE. Par M. BERTHELOT, Membre de l'Institut. Paris, George Steinheil, Editeur.

As the title indicates, this book is not a complete history of alchemy. The author's purpose is to show how the problem of transmutation of common into precious metals came to be suggested to the minds of men, and where the theories and practices of alchemy came from. The author says (p. 2): "The history of alchemy is very obscure. It is a science apparently without origin, which appears suddenly about the time of the fall of the Roman Empire, and which develops throughout the Middle Ages, amid mysteries and symbols, remaining all the while a secret and persecuted doctrine, under the ban of the Church. Its real scholars are confounded with the deluded, with charlatans, and sometimes with the unprincipled. This history deserves to be taken up, in its whole extent, according to the methods of modern critical investigation. Without undertaking so extensive a research, which would require the whole lifetime of a scholar, I desire to attempt

to penetrate the mystery of the origin of alchemy, and to show by what lines it is connected with the industrial processes of the ancient Egyptians, with the speculative theories of the Greek philosophers, and with the mystic dreams of the Alexandrians and Gnostics."

The work is divided into four books, as follows: 1, the sources, 2, the persons, 3, the facts, 4, the theories.

In the first book is given the historical evidence to show that among the ancient Egyptians, the Chaldeans, the Greeks, and the Jews, there existed the germs of alchemy, partly in the form of facts involved in industrial processes, such as metallurgy, partly in the form of speculative ideas and of mystic and religious theories. It appears that alchemy was first practiced in Egypt as early, probably, as the second century of our era, and that it resulted from the fusion, at Alexandria, of the learning of Greece with that of Egypt and Chaldea. From Egypt came the practical features, mingled with something of the religious or mystic; from Chaldea, more of the latter than of the former; from Greece, portions of philosophy peculiar to the Ionic and Platonic school, pertaining to the constitution of matter. The first alchemists were Gnostics (a name applied to the followers of a system which was a fantastical combination of oriental and Greek philosophy with the doctrines of Christianity). Gnosticism played an important part in all the East, and particularly in Alexandria in the second century of our era.

From the following (pp. 52–3) it is to be inferred that alchemy, once started, spread rapidly over the world: "Alchemy appeared in China in the third century, at the same period in which it flourished in Egypt among the Alexandrians. . . . They find in the great encyclopedia *Pei-ouen-yun-fou*, which in China possesses great authority, this very plain statement: 'The first who refined the *Tan* (transmutation of metals) was one named *Ko-hong*, who lived at the time of the dynasty of *Ou*.' The dynasty of *Ou* reigned from 222 A. D. to 277 A. D. It was, then, about the middle of the third century when the Chinese commenced to practice alchemy."

The remainder of the first book is given to a description of the more important manuscripts referred to for historical evidence. M. Berthelot has not confined himself to consulting the statements found in the histories of Kopp and Hoefer, but he has delved in the great libraries of Europe and has succeeded in bringing forth the most ancient documents known, bearing on the subject of alchemy, the principal contents of which now come to us in this volume for the first time.

In the second book is stated what is known about those alchemists whose names appear in the manuscripts. Some of these personages are purely mythical; some assumed the names of well-known historical personages, and in this way we account for the appearance in the *rôle* of alchemists of such names as Moses,

Queen Cleopatra, Plato, Aristotle, etc. The Greek alchemists, properly so called, are more tangible individuals, such as Zosimus, Africanus, Olympiodorus, etc., considerable portions of whose writings have come down to us.

The third book is devoted to a statement of such practical chemical facts as were known to the Egyptians, such, for example, as concerned the preparation and coloring of the metals and their alloys, and the preparation of artificial precious stones. The very little known in regard to the old Egyptian laboratories is stated in this connection.

The last book contains a statement of such theories of the Greek philosophers as formed the germs of the theories of the alchemists; and, finally, these theories of the alchemists are compared with certain ideas prevailing to-day in regard to the constitution of matter. The ideas of the first alchemists are pretty clearly shown to have been closely connected with the philosophy of Plato, and particularly with the theories expressed in Plato's Timaeus.

The author's general conclusions as to the origin and growth of alchemy may be summed up as follows: The first ideas of transmutation of metals came from Egypt and Chaldea, and their origin is lost in antiquity, probably very remote. The Greeks of Egypt transformed these practices into a theory, half scientific, half mystic, just about as they did in case of astrology. From Egypt alchemy was carried to Constantinople in the course of shifting events, and about the seventh or eighth century was transmitted to the Arabs. Finally, the Arabs of Syria and of Spain carried alchemy to Europe.

While M. Berthelot's work has not revealed any startling discoveries, the results of his research have furnished a more satisfactory basis for the historical study of alchemy than we have hitherto possessed. Many connections which were previously only suspected or guessed at may now be regarded as having a fairly good historical basis. M. Berthelot devoted much of his time for six years to this study, the results of which are given in this book. We can understand something of the student-heroism of his undertaking when he tells us that he has read the original passages of all the Greek and Latin references, and, in order to do this, he had to renew his knowledge of Greek by rubbing off the accumulation of forty years' rust.

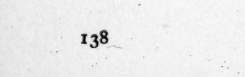
The heavy paper, the generous margins, and the large clear type combine to make a volume which will delight the eye of any one who looks for beauty of this kind in books. An appendix furnishes details of interest in regard to several of the manuscripts cited. Then comes a carefully prepared analytical table of contents, and finally an extremely elaborate index, first of names and then of words.

L. L. Van Slyke.

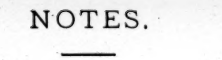
NOTES.

A New Synthesis of Uric Acid.

During the past few years much notable work has been accomplished which had for its end the solution of the problem of the constitution of uric acid. Fittig[1] proposed the symmetrical formula

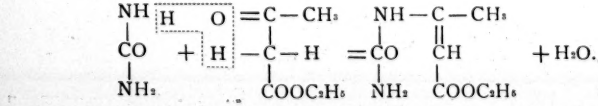


to represent the structure of the substance; on the other hand Medicus[2] put forward as a nearer approach to the truth the unsymmetrical formula



. The work of Fischer[3] has added much to the evidence in favor of the latter conception; while the brilliant syntheses of Horbaczewski,[4] although of the greatest interest, yet on account of the very meagre yield and of the difficulty encountered in attempting to explain the transformations brought about, cannot be said to have hastened much the final solution of the problem. A new method of synthesis has been described by Behrend and Roosen[5] which seems to show that the formula suggested by Medicus is in all probability correct. The following is a short abstract of the paper of these investigators which describes the synthesis of isobarbituric acid by Behrend[6] as well as the conversion of the latter into uric acid.

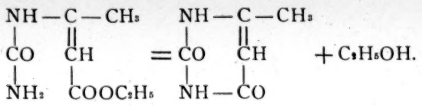
(1) Heated together, ethyl acèto-acetate and urea combine with loss of the elements of water to form the ethyl ether of β-uramido-crotonic acid:



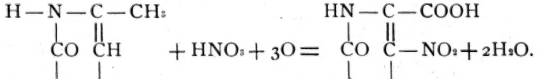
(2) Through saponification by means of caustic potash this ether

[1] Grundriss d. org. Chemie, 10te Aufl. s. 309.
[2] Ann. Chem. (Liebig) **175**, 230.
[3] Ber. d. chem. Ges. **17**, 1776.
[4] Monatsh. Chem. 1882, 796; 1885, 356; 1887, 201, 584.
[5] Ann. Chem. (Liebig) **251**, 235. [6] Ibid. **229**, 39.

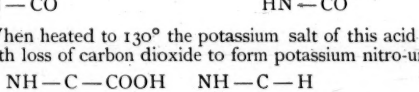
is converted into the potassium salt of β-uramidocrotonic acid, and the acid when in the free condition is decomposed into water and the anhydride, methyluracil:



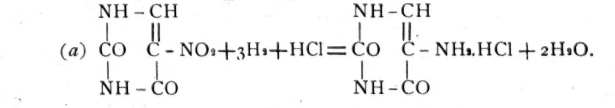
(3) Fuming nitric acid converts this anhydride into nitro-uracil-carbonic acid:

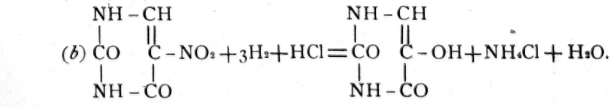


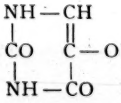
(4) When heated to 130° the potassium salt of this acid breaks down with loss of carbon dioxide to form potassium nitro-uracil:



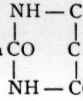
(5) Upon reduction by means of tin and hydrochloric acid, nitro-uracil is converted partly into amido-uracil, partly into isobarbituric acid.



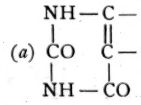
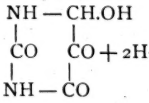


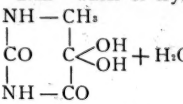
According to Behrend,[1] the condition  is not a stable one, and the rearrangement which the substance immedi-

[1] Ann. Chem. (Liebig) **229**, 40.

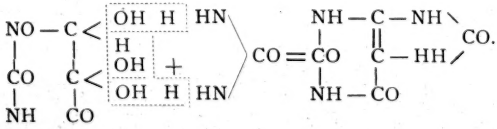
ately undergoes results in the formation of an acid whose constitution is to be represented by the formula  .

(6) Behrend and Roosen now find that this isobarbituric acid is, upon treatment with bromine water, oxidised to isodialuric acid, $C_4H_4N_2O_4 + 2H_2O$, for which the two possible formulas are:

(*a*)  and (*b*)  .

The action of hydroxylamine upon isodialuric acid leads the authors to conclude that the formula (*b*) is the correct representation of the structure of the compound. Since, however, in the hydrated form of the acid, one of the molecules of water appears to be rather "water of constitution" than "water of crystallisation," they make use of the formula  to express the constitution of the hydrated acid. Amidouracil, upon oxidation by means of bromine water, yields the same product, isodialuric acid.

(7) Finally, in the presence of sulphuric acid, a mixture of isodialuric acid and urea combine, water being abstracted, with production of uric acid:



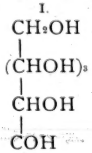
Experiments upon the comparative solubility of the natural and synthetically prepared uric acid in water were made by the authors, and salts of sodium, potassium, calcium, barium, and magnesium were obtained from both varieties of acid. Allantoïn was also prepared from the natural as well as from the synthetically obtained acid. A careful study of the comparative behavior of these derivatives and of the two acids showed that they are identical.

W. W. RANDALL.

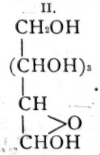
Constitution of Dextrose.

Dextrose is usually regarded as an aldehyde alcohol containing five hydroxyl groups. There is, however, another view possible, as first suggested by Fittig, and recently advocated by Tollens, according to which dextrose is the inner anhydride of a heptacid alcohol.

I.



II.



If this anhydride, as represented in formula II, be conceived as taking up water to form the heptacid alcohol, and this then again loses water, the result would be an aldehyde of formula I. This would explain the reactions of dextrose in which it seems to be an aldehyde, and the conduct of dextrose towards phenylhydrazine could not be regarded as a proof of the correctness of formula I.

In order to decide which of these two formulas is the correct one, Z. H. Skraup[1] makes use of a pentabenzoyl derivative of dextrose, which he describes in another article. If formula I be correct, then the pentabenzoyl derivative must be an aldehyde and will show all the characteristic conduct of an aldehyde; that is, it should yield a pentabenzoyl gluconic acid and also a pentabenzoyl dextrose phenylhydrazine compound. If on the other hand formula II be correct, the pentabenzoyl derivative could neither yield a hydrazine derivative nor a carbonic acid. It is hence possible to determine the constitution of the dextrose pentabenzoate and of dextrose itself, by the action of phenylhydrazine and by the action of oxidising agents upon pentabenzoyl dextrose.

Skraup found it impossible to obtain either a normal phenylhydrazine derivative or a phenylpentabenzoyl glucosazon from the dextrose pentabenzoate by treatment with phenylhydrazine. The reaction with phenylhydrazine therefore affords no proof of the correctness of the aldehyde formula for dextrose.

On oxidation with potassium permanganate, as well as with nitric and chromic acids, no pentabenzoyl gluconic acid was obtained.

These facts make it exceedingly improbable that the pentabenzoyl dextrose is an aldehyde, and lead to the Fittig-Tollens formula for dextrose; nevertheless it cannot be denied that dextrose conducts itself in many of its reactions as an aldehyde, and this necessitates the assumption of a transition of the two forms in one or the other direction.

The peculiar optical property of bi-rotation of dextrose is also in strict accord with this idea of a molecular change.

[1] Monatsh. Chem. 8, 401.

It is well here to remember that the crystallised dextrose $C_6H_{12}O_6 + H_2O$ has exactly the composition of the heptacid alcohol, and it is by no means proved that in this compound the water is present as water of crystallisation. In fact an observation of Soxlet, confirmed by Skraup, that anhydrous dextrose can be crystallised from water in the anhydrous condition, makes the existence of the water of crystallisation in the so-called hydrate of dextrose very doubtful. Skraup endeavors to show that the anhydrous dextrose and the hydrated dextrose differ from each other in their reactions, but without success. When the two substances are treated with phenylhydrazine, he obtains from both an α and a β modification of the dextrose phenylhydrazine. After proving beyond any doubt that these two modifications exist, he states that both result from a replacement of an atom of oxygen, and that this can only be explained on the assumption that the dextrose reacts in different forms with the phenylhydrazine, in the first case as the inner anhydride and in the second as the aldehyde or heptacid alcohol.

Since both the α and the β modification yield the phenyl glucosazon when treated with an aqueous solution of phenylhydrazine acetate, the constitution of the anhydride form of dextrose is fixed. It must be an α anhydride, as shown in formula II.

W. R. Orndorff.

The Molecular Weight of Starch.

Brown and Morris[1] have successfully applied the method of Raoult to the determination of the molecular weights of some of the carbohydrates.

Starch (the variety known as *soluble starch*, prepared by treating ungelatinised potato-starch with hydrochloric acid of 7.5 per cent.) was found to have but a very slight influence upon the freezing point of water, the depression produced corresponding to a molecular weight somewhere between 20,000 and 30,000.

It was at first thought that substances of such a highly colloidal nature as starch might exert only a slight influence on the freezing point of water. Arabinic acid, however, a substance of very marked colloidal properties, exerted a strong influence on the freezing point of water. It seemed probable, therefore, that the small influence observed in the case of soluble starch was really due to the large size of the molecule.

A study of the action of diastase on the starch showed that the act of hydrolysis stops when the amount of dextrin produced corresponds to *one-fifth* the weight of the amount of starch used. The reaction would be expressed thus:

$$\underset{\text{Starch.}}{5C_{12}H_{20}O_{10}} + 4H_2O = \underset{\text{Dextrin.}}{C_{12}H_{20}O_{10}} + \underset{\text{Maltose.}}{4C_{12}H_{22}O_{11}}.$$

The evidence is almost conclusive that the production of maltose

[1] J. Chem. Soc. (London) **56** (1889), 462.

and dextrin in the above reaction is due to molecular degradation of the starch by hydrolysis. This being the case, it follows that *the molecule of the stable dextrin of the above equation is one-fifth of the size of the soluble starch molecule from which it has been derived.*

The molecular weight of this dextrin was found to correspond approximately to 6480, the figure required by the formula $20(C_{12}H_{20}O_{10})$. The formula of soluble starch would, consequently, be five times this value, or $5(C_{12}H_{20}O_{10})_{20}$. This would give a molecular weight of 32,400, which is in accordance with the approximation (20,000–30,000) obtained by estimating the molecular weight of soluble starch directly. R. DE ROODE.

Chemical Examination of an Ancient Sceptre.

M. Berthelot has recently discussed the question of the manufacture of bronze by ancient peoples. As copper is widely distributed in nature, the use of that metal might have been expected. Tin, the other constituent of bronze, is on the contrary found in but few localities, and even these are of comparatively difficult access. The positive statements, therefore, which have hitherto been made concerning the general use of bronze by prehistoric peoples have for a long time puzzled those who have given the matter attention. Archæologists agree that the use of unalloyed copper for arms and utensils preceded that of bronze, but the date of the introduction of the alloy of copper and tin has never been satisfactorily settled. Among the many so-called bronze implements contained in collections of Egyptian antiquities, one, the sceptre of Pepi I, a king of the 6th dynasty, archæologists have agreed belongs to an age between 35 and 40 centuries before the Christian era. From the interior of this sceptre some small fragments of the metal were dislodged, and sent by the director of the British Museum to M. Berthelot. An analysis of these particles failed to indicate the presence of even a trace of tin or of zinc. From this M. Berthelot argues that bronze was unknown at this epoch, as otherwise it would have been used in this instance instead of the softer copper. He comes finally to the conclusion, based upon this and other proof, that the art of bronze manufacture has not been known at any rate for more than from fifty to sixty centuries.—(*Ann. Chim. Phys.*) W. W. RANDALL.

On the Arrangement of the Atoms in Space in Molecules containing Nitrogen.

A. Hantzsch and Alfred Werner[1] have proposed an interesting extension of the conceptions of Le Bel, van't Hoff and Wislicenus, with the object of explaining certain cases of isomerism observed among compounds containing nitrogen which cannot be accounted

[1] Ber. d. chem. Gesell. **23**, 11 (1890).

for by the usual conceptions of stereo-chemistry. K. Auwers and V. Meyer have shown that there are two compounds of the structure $C_6H_5-C(NOH)-C(NOH)-C_6H_5$. They have suggested that there may be a kind of single union between carbon atoms which does not permit of free rotation, and that the stereo-chemical formulas of the two compounds may be

$$C_6H_5-C=NOH \quad \text{and} \quad C_6H_5-C=NOH$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad |$$
$$C_6H_5-C=NOH \quad\quad HON=C-C_6H_5.$$

Hantzsch and Werner, however, think it more probable that the seat of the isomerism is to be found in the relations of the nitrogen atom to the rest of the molecule. We may conceive of the nitrogen atom being situated at one of the solid angles of a tetrahedron and exerting its affinities in the direction of the three edges of the tetrahedron. Then, whenever a nitrogen atom is united to a carbon atom by two bonds, a possibility of isomerism would exist. Thus, take any compound $YXC=NZ$. Two arrangements in space are possible, viz.:

$$Y-C-X \quad \text{and} \quad Y-C-X$$
$$\quad\| \quad\quad\quad\quad\quad\|$$
$$N-Z \quad\quad\quad\quad Z-N,$$

and these bear to each other very much the same relations as the the two compounds:

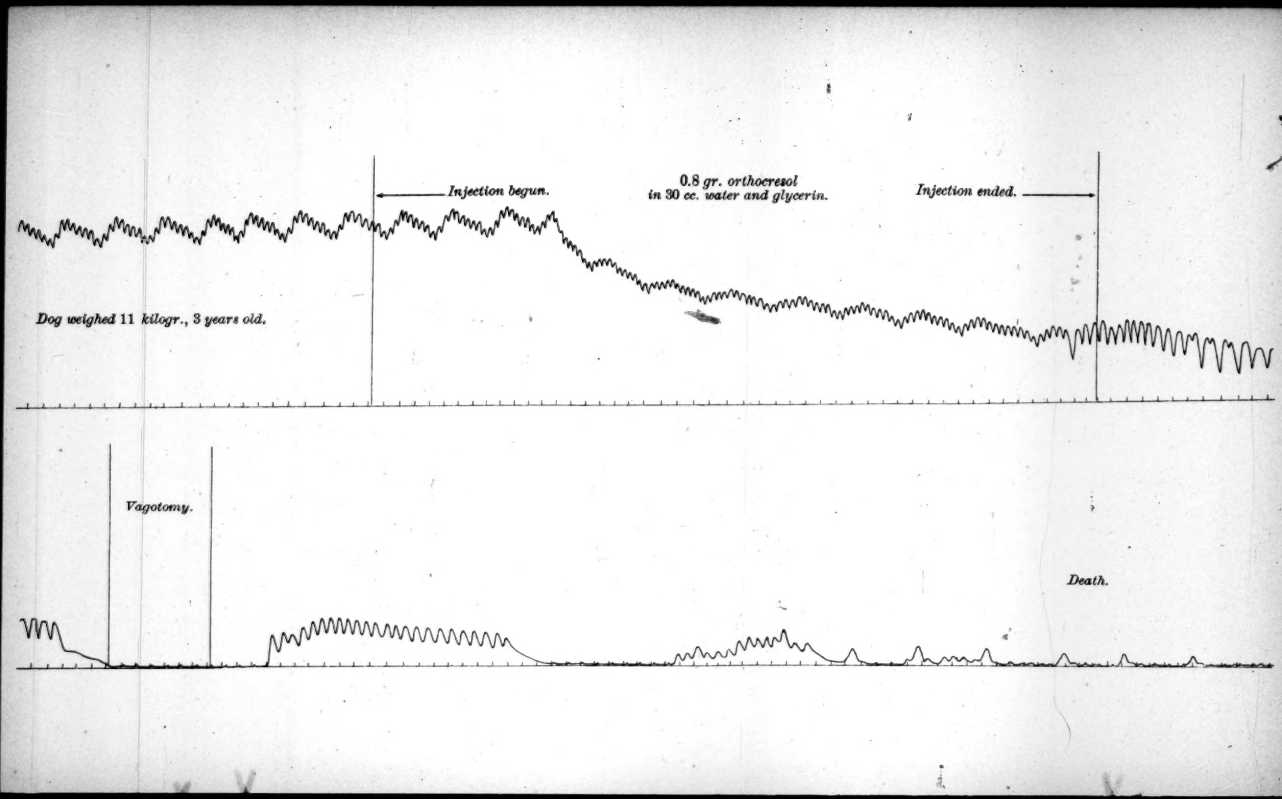
$$Y-C-X \quad \text{and} \quad Y-C-X$$
$$\quad\| \quad\quad\quad\quad\quad\|$$
$$Z'-C-Z \quad\quad\quad\quad Z-C-Z'.$$

According to this view, three compounds of the formula $C_6H_5-C(NOH)-C(NOH)-C_6H_5$ are possible. These are represented by the formulas:

I. $C_6H_5-C(HON)-C(NOH)-C_6H_5$ II. $H_5C_6-C(NOH)-C(HON)-C_6H_5$ III. $H_5C_6-C(HON)-C(HON)-C_6H_5$.

This kind of isomerism is also possible in the case of compounds of the formula $\begin{matrix}NX\\ \|\\ NY\end{matrix}$, and an example of this kind seems to be that of the two trinitroazotoluenes $CH_3(NO_2)H_2C_6N=NC_6H_2(NO_2)_2CH_3$, which, according to Janowski, have the same structure.

I. R.


Injection begun.
0.8 gr. orthocresol
in 30 cc. water and glycerin.
Injection ended.
Dog weighed 11 kilogr., 3 years old.
Vagotomy.
Death.